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PhD Thesis

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DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

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Development and implementation of a framework for sustainable carbon dioxide capture and utilization processes

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Preface

This dissertation titled “Sustainable Process Design with Process Intensification: Development and implementation of a framework for sustainable carbon dioxide capture and utilization processes" is submitted to the Technical University of Denmark (DTU) in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Ph.D.) in Chemical Engineering. This research project titled “Sustainable Process Design with Process Intensification" has been carried out from October 2014 until December 2017 at the KT Consortium at the department of Chemical and Biochemical Engineering of the Technical University of Denmark under the supervision of Professor Rafiqul Gani and co-supervision of Professor John M. Woodley.

First, I would like to thank my supervisors Rafiqul Gani and John M. Woodley for their support throughout this project. I appreciate all the help, support and guidance throughout these three years. You have been great supervisors and have helped guide me through this project. In addition, I would like to thank all of my friends and colleagues at DTU. I would like to thank Mariona Bertran. Thanks for being such an understanding and helpful colleague and office mate. It has been great sharing an office with you and I am thankful for having a “sounding board” for ideas and when I was stuck. I would also like to thank all my colleagues at the KT Consortium. I have enjoyed these three years. To all my other colleagues in PROSYS and the rest of the Department of Chemical and Biochemical Engineering, you have all helped make these three years unforgettable. Working with SAT and the KT Staff Club has helped balance the academic with some fun social and cultural events. I am glad to call many of you my friends!

Finally, I would like to thank my friends and family in Germany, Denmark and the US for supporting me on this journey. To my parents, thank you for being there despite the distance. I know you are only a skype call away if I need anything. To my siblings, thanks for the crazy memories to take my mind off of things when I

need it. To Mia, my best friend, thanks for understanding and being there for me, even though we don't get to see each other enough. We have known each other for so long, I can't wait to see where we are headed! Most of all, I want to thank Sebastian for being there for me no matter what. When I need someone to listen or when I need someone to distract me, I know that I can count on you. These three years haven't always been easy and I couldn't have done it without you.

Thanks!

Rebecca Frauzem
Kgs. Lyngby, 2017

Abstract

Due to environmental concerns, greenhouse gas emissions, particularly carbon dioxide, need to be reduced. There are numerous methods being discussed, one of which is carbon dioxide capture and utilization (CCU). Carbon dioxide capture and utilization removes the carbon dioxide from the offgas streams and transforms it into commercial products, for example the conversion to value-added chemicals. While CCU is promising, especially as the commercial products provide an economic incentive, the sustainability needs to be ensured. Assuring the sustainability of carbon dioxide capture and utilization processes is a challenge as the energy requirements of result in indirect emissions that should not exceed the utilization. In this work, therefore, a framework for the sustainable design of carbon dioxide capture and utilization (with a focus on conversion) processes is developed and implemented. The developed framework adopts a 3-stage approach for sustainable design, which is comprised of: (1) synthesis, (2) design, and (3) innovation. In the first stage, the optimal processing route is obtained from a network via a superstructure-based approach. This stage incorporates a structured database for the storage and retrieval of data, reaction path synthesis for the generation of reaction pathways and products, and a user interface, Super-O, which facilitates the implementation of Stage 1 of the framework. Then, the output of this stage is used as the input to the second stage, where the optimal route is rigorously designed, simulated and analyzed. Stage 2 provides detailed equipment design and stream information, which is used in the analysis to provide targets for improvement. In Stage 3, the targets are addressed by finding innovative alternatives via hybrid methods, process integration and process intensification. The end result is a more sustainable carbon dioxide capture and utilization process.

The developed framework is then applied to the design of sustainable processes using carbon dioxide captured from a coal-fired power plant (as these represent almost 30% of global emissions). In the first stage, seven scenarios are considered

to evaluate the influence of different parameters (such as prices and conversion) in finding the optimal processing route(s). The results show a trade-off in the reduction of carbon dioxide and the profit for the different routes. From Stage 1, four processes are considered and are designed and simulated in detail:

1. Dimethyl ether from methanol via combined reforming
2. Dimethyl ether from methanol via direct hydrogenation
3. Dimethyl carbonate via ethylene carbonate and methanol from combined reforming
4. Dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation.

Through the analysis of the processes, it can be seen that the methanol distillation and the dimethyl carbonate downstream separation contribute to large amounts of the utility consumption and therefore costs. Therefore, the reduction of the utility consumption of the methanol distillation and dimethyl carbonate downstream process are targeted for improvement. In Stage 3, the targets are addressed by introducing a hybrid distillation-membrane process and an intensified, reactive distillation dimethyl carbonate process. The result is four improved, more sustainable processes for the production of dimethyl ether and dimethyl carbonate from carbon dioxide. However, while it is possible to design carbon dioxide reducing processes, the amount of emissions that can be offset by these processes is small. Therefore, these carbon dioxide capture and utilization or conversion processes should be considered in conjunction with methods to improve efficiency and other alternative, sustainable processes.

Resumé på dansk

Af miljømæssige årsager er der et behov for at reducere emissioner af drivhusgasser – dette gælder især kuldioxid. Der er adskillige metoder til dette formål, der diskuteres i denne afhandling, hvoraf en er kuldioxidopsamling og -udnyttelse (eng. Carbon capture and utilization, CCU). Kuldioxidopsamling og -udnyttelse fjerner kuldioxid fra affaldsstrømme/røg og omdanner det til kommercielle produkter, f.eks. via værdiskabende kemikalier. Selvom CCO er lovende, især pga. de kommercielle produkters økonomiske incitament, skal bæredygtigheden sikres. Det er en udfordring at sikre bæredygtigheden af CCU, idet processernes energibehov resulterer i indirekte udledninger, som ikke må underminere gevinsten ved CCU. I dette arbejde udvikles og implementeres derfor en ramme for bæredygtig udformning af CO_2-opsamling og -udnyttelse (med fokus på omdannelse). Den udviklede ramme anvender en 3-trins tilgang til bæredygtigt design, der består af: (1) syntese, (2) design og (3) innovation. I det første trin opnås den optimale omdanneslesrute fra et netværk via en superstruktur-tilgang. Dette trin inkorporerer en struktureret database til lagring og hentning af data, reaktionsvejssyntese til generering af reaktionsveje og produkter samt en brugergrænseflade, Super-O, som faciliterer gennemførelsen af trin 1 af rammen. Derefter anvendes resultatet af dette trin som input til trin 2, hvor den optimale rute på detaljeret vis designes, simuleres og analyseres. Trin 2 resulterer således i detaljeret udstyrsdesign og strøminformation, som bruges til at analysere mål for forbedringer. I trin 3 adresseres målene ved at finde innovative alternativer via hybrid-metoder, procesintegration og procesintensivering. Slutresultatet er en mere bæredygtig kuldioxidopsamling- og udnyttelsesproces.

Den udviklede ramme anvendes på udformningen af bæredygtige processer til kuldioxid opsamlet fra et kulfyret kraftværk (fordi de repræsenterer næsten 30% af de globale emissioner). I første trin betragtes syv scenarier for at vurdere indfly-

delsen af forskellige parametre (såsom priser og stofomsætning) for at finde de(n) optimale behandlingsrute(r). Resultaterne viser en afvejning mellem reduktionen af kuldioxid og profitten for de forskellige ruter. I trin 1 betragtes følgende fire processer med henblik på design og simulering:

1. dimethylether fra methanol via kombineret reformering
2. dimethylether fra methanol via direkte hydrogenering
3. dimethylcarbonat via ethylencarbonat og methanol fra kombineret reformering
4. dimethylcarbonat via ethylencarbonat og methanol fra direkte hydrogenering.

Ud fra analyse af processerne kan det konkluderes, at methanoldestillationen og dimethylcarbonat-nedstrømsadskillelsen bidrager til store mængder af utilityforbrug og dermed omkostninger. Derfor er reduktionen af utilityforbrug i methanoldestillationen og dimethylcarbonat-nedstrømadskillelse udvalgt til undersøgelser for mulige forbedringer. I trin 3 behandles de udvalgte forbedringsforslag ved at indføre en hybrid destillationsmembranproces og en intensiveret, reaktiv destillationsdimethylcarbonatproces. Resultatet er fire forbedrede, mere bæredygtige processer til produktion af dimethylether og dimethylcarbonat fra kuldioxid. Imidlertid er det muligt at konstruere kuldioxidreducerende processer, men mængden af emissioner, som kan kompenseres af disse processer, er lille. Derfor bør kuldioxidopsamling og -udnyttelse betragtes sammen med metoder til forbedring af effektiviteten og andre alternative, bæredygtige processer.

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Nomenclature

Symbol	Definition	Units
Roman symbols		
A	Linearization coefficient	
B	Linearization coefficient	
C	Costs	$\frac{\text{USD}}{\text{hr}}$
C^T	Matrix of cost coefficients	
f	Component flow	$\frac{\text{kg}}{\text{hr}}$
F	Total flow	$\frac{\text{kg}}{\text{hr}}$
$FPOINT$	Point flow	
F_{obj}	Objective function	$\frac{\text{USD}}{\text{hr}}$
g	Added or removed component flow	$\frac{\text{kg}}{\text{hr}}$
INT	Number of intervals	
inv	Investment costs	USD
M	The big M variable	
MW	Molecular weight	$\frac{\text{kg}}{\text{kmol}}$
N	Interval number	
P	Prices	$\frac{\text{USD}}{\text{hr}}$
$piece$	Binary variable for linearization interval	
R^n	all real numbers	
S	Sales	$\frac{\text{USD}}{\text{hr}}$
$source$	Source	
SS	Superstructure connection binary variable	
x	Continuous variables	
y	Binary variable (for interval selection)	
Z	General function	

Symbol	Definition	Units
Greek symbols		
β	Utility addition factor	$\frac{\text{kWh}_{\text{ut}}}{\text{kg}}$
δ	Waste separation factor	$\frac{\text{kg}_{\text{out}}}{\text{kg}_{\text{in}}}$
η	Transportation distance	$\frac{\text{km}}{\text{kg}}$
γ	Stoichiometric coefficient	
μ	Mixing mass fraction	$\frac{\text{kg}_{\text{ii}}}{\text{kg}_{\text{i}}}$
ω	Binary variable for blender	
ϕ	Mass fraction	
σ	Product separation factor	$\frac{\text{kg}_{\text{out}}}{\text{kg}_{\text{in}}}$
τ	Project lifetime	y
θ	Conversion	
υ	Allocation of interval to step	
Superscripts		
^{CAP}	Capital costs	
^{CHEM}	Chemicals	
^{D}	Dissaggregated	
^{IN}	Inlet stream	
^{M}	After mixing task	
^{OUT}	After product separation task	
^{P}	Primary stream	
^{PROD}	Product	
^{R}	After reaction task	
^{RAW}	Raw materials	
^{S}	Secondary stream	
^{TR}	Transportation	
^{UT}	Utilities	
^{W}	After waste separation task	
^{WASTE}	Waste	
^{1}	Utility mixing point 1	
^{2}	Utility mixing point 2	
^{3}	Utility mixing point 2	
Subscripts		
$_{i}$	Component	
$_{ii}$	Mixing component	
$_{j}$	Index for linearization	

Symbol	Definition	Units
k	Starting interval	
kk	Ending interval	
r	Reaction	
$react$	Reactant	
Abbreviations		
BAU	Business as usual	
CAMD	Computer Aided Molecular Design	
CAPEX	Capital costs	USD
CCS	Carbon dioxide capture and storage	
CCU	Carbon dioxide capture and utilization	
CCUS	Carbon dioxide capture, utilization and storage	
GWP	Global warming potential	
kg	kilogram	
LCA	Life cycle assessment	
LHHW	Langmuir-Hinshelwood-Hougen-Watson	
M	Thousand	
MI(N)LP	Mixed-Integer Non-Linear Program	
MM	Million	
OPEX	Operating expenditures	
PI	Process Intensification	$\frac{\text{USD}}{\text{y}}$
PSIN	Processing Step-Interval Network	
RPS	Reaction path synthesis	
t	ton	
USD	U.S. Dollar	
Chemical abbreviations		
CO	CO Carbon monoxide	
CO_2	CO_2 Carbon dioxide	
DMC	$C_3H_6O_3$ Dimethyl carbonate	
DME	C_2H_6O Dimethyl ether	
EC	$C_3H_4O_3$ Ethylene carbonate	
EG	$C_2H_6O_2$ Ethylene glycol	
EO	C_2H_4O Ethylene oxide	
EtOH	C_2H_5OH Ethanol	
H_2O	H_2O Water	
MEA	C_2H_7N Monoethyl amine	
MeOH	CH_3OH Methanol	

Symbol	Definition	Units
NH3	NH_3 Ammonia	
NOx	Nitrous oxides	
PC	$C_4H_6O_3$ Propylene carbonate	
PG	$C_3H_8O_2$ Propylene glycol	
PO	C_3H_6O Propylene oxide	
SOx	Sulfur oxides	
Urea	CH_4N_2O Urea	

Chapter 1

Introduction

Summary and significance:

Due to population growth and continued development, there is an increasing amount of waste and emissions being produced. These emissions result in environmental concerns, including global warming, that need to be addressed and sustainable development needs to be ensured. Greenhouse gases are the cause for global warming and need to be mitigated; these gases consist primarily of carbon dioxide, at over 75%. Carbon dioxide capture and utilization, particularly conversion, is one method of addressing these emissions. This chapter provides an overview of the current environmental situation, the emissions that need to be reduced, and what methods can be used to achieve this, primarily carbon dioxide capture and utilization. In addition, the objective of the work and structure of the thesis are detailed.

Outline:

As a result of rapid population growth over the past years, reaching almost 8 billion, there are increasing concerns about the state of the planet (UNFPA, 2016b). Climate change issues are associated with this increasing population (UNFPA, 2016a); there is an increasing demand on natural resources (food, water, minerals, etc.) and more manufacturing and energy consumption, resulting in increased waste and emissions. As part of these emissions, greenhouse gases are linked to global warming. Global warming is the increase in the global temperature due to the increasing concentration of greenhouse gases in the atmosphere (Dincer, 2009). These greenhouse gases include carbon dioxide, methane, water vapor, nitrous oxide and various hydrofluorocarbons (HFCs, etc.). In the year 2010, greenhouse gas emissions reached 49 Gigatonnes of carbon dioxide equivalents per year and trends show this increasing by 1 Gigatonne per year (IPCC, 2014). The threshold concentration of carbon dioxide equivalents of 400 parts per million (ppm) was already passed in 2016 (Keeling et al., 2005); this corresponds to a 1.5 degrees Celcius global temperature rise (IPCC, 2014). The new threshold has been set to 450 ppm, representing a global temperature rise of 2 degrees Celcius (IPCC, 2014). If this cannot be met, the temperature rise will continue to cause irreparable damage to the earth and its ecosystem. While greenhouse gases are naturally emitted to the atmosphere, these are also counterbalanced by other natural processes. However, due to human activities, there is an imbalance resulting in the environmental climate concerns. While all greenhouse gases needed to be addressed (methane, NOx and HFCs are also harmful greenhouse gases), carbon dioxide represents the largest constituent at almost 80 percent of greenhouse gases and the need to reduce the amount of carbon dioxide in the atmosphere has become an urgent matter.

1.1 Emission sources

The source, quantity and purity of the emissions is important to effectively target and reduce the amount of carbon dioxide in the atmosphere. Carbon dioxide containing emissions come from different economic sectors IPCC (2007). These economic sectors produce emissions in varying processes, including processes to produce energy, products, or serve other needs. In addition to the economic sector of the sources, the carbon source used in the process alters the emission composition. When the process uses coal versus natural gas, for example, the emissions contain a higher content of carbon dioxide because coal contains a larger quantity of impurities. Therefore, emissions can be categorized as follows:

1. Process type (i.e. power generation, steel industry, cement production)

2. Specific process (i.e. power plant)

3. Carbon source (i.e. coal)

1.1.1 Emission location, amount and purity

While the category of the emissions is important for organizing the information, the amounts and purity of the emissions in different locations need to be considered for proper design of capture and utilization processes. While there are emissions from transportation and other transient processes that need to be reduced, in this work, stationary emissions coming from a fixed location are considered. The categories listed in Section 1.1 span across locations. However, at the different locations, the specific amount and purity vary. The purity is the most important as it defines whether purification is necessary to make the carbon dioxide applicable for utilization. The purity of the emissions can be split into three qualities:

1. High quality emissions (greater than 85% carbon dioxide)

2. Medium quality emissions (between 20 and 85% carbon dioxide)

3. Low quality emissions (less than 20% carbon dioxide)

1.1.1.1 High purity sources

Only 430 million tons per year of emissions come from high purity industrial sources (IPCC, 2014). The amounts of these emissions at various sources are (Zakkour and Cook, 2010):

- between 0.5 and 1 million tons of carbon dioxide per year at sites for natural gas production.
- around 0.2 million tons of carbon dioxide per year from ethylene oxide production sites.
- between 1.6 and 3.8 tons of carbon dioxide per ton of ammonia produced, where the hydrogen production contributes a significant amount, between 1.15 and 2.6 tons of carbon dioxide per ton of hydrogen.

1.1.1.2 Medium purity sources

A much higher amount of emissions, around 30%, comes from medium purity sources. These sources include some metal and cement manufacturing industries. Annually, 930 million tons of carbon dioxide come from the cement industry alone.

These emissions have concentrations of around 20% carbon dioxide in amounts of 0.8 million tons per year per site (IPCC, 2005). The other emissions are NOx, SOx, dust, metals and others. The exact composition depends on the location and the fuel source used.

1.1.1.3 Low purity sources

The largest contributors to emissions of carbon dioxide are low purity. Over 50% of these come from power plants alone (IPCC, 2005). The rest come from steel mills and other production processes. Similar to medium purity sources, the other compounds include NOx, SOx, other hydrocarbons, water and nitrogen. The amount of low purity emissions per site depend greatly on the exact process. For power plants, the largest amount comes from coal-fired sources, averaging at 3.94 million tons per year (IPCC, 2005). The smallest comes from fuel oil sources.

1.1.1.4 Availability and locality of emissions

Carbon dioxide containing emissions are a global issue. The location and amount of the given source, however, need to be considered. While globally there are approximately 50 Gigatonnes of carbon dioxide equivalents per year being emitted, only about 60% of these can be addressed by carbon capture and storage (IPCC, 2014) with the remainder being from non-stationary sources that cannot be easily captured. The availability and locality of the emissions from these stationary sources varies. Emissions are available in every country. However, generally the sources are concentrated in industrial and manufacturing areas and power generation facilities. As mentioned previously, depending on the exact source, the amount and purity varies. The high purity sources are the least available and also in the lowest amount per year. However, as these are generally located at chemical plants, the capture and utilization of these emissions can be more easily realized. Medium and low purity emissions are prevalent and present in large quantities. For these emissions, the challenge is utilizing all the emissions from a given source, as the utilization capacity may not match. Despite the global availability of the emissions, the exact location and amount needs to be considered for the design of carbon dioxide reduction technology.

1.2 Reduction methods

There are numerous ways of addressing emissions from the different sources. There are three primary methods considered:

1. Improve process efficiency
2. Carbon dioxide capture and storage/sequestration
3. Carbon dioxide capture and utilization (including conversion)

All of these methods will play an important role in reducing the atmospheric carbon dioxide concentration. Carbon dioxide capture involves the removal of carbon dioxide from process streams, especially flue gas streams (Wilcox, 2012). Storage or sequestration involves the transportation and storage of the compressed, captured carbon dioxide gas in tanks, in geological formations or under sea beds (Wilcox, 2012). Carbon dioxide utilization is the reuse of the separated carbon dioxide to produce commercial products (Song, 2002). Carbon dioxide capture is necessary in order to address all types of emissions with higher concentrations and lower concentrations. Then, the separated carbon dioxide is either stored or utilized. While there are advantages and disadvantages to both, carbon dioxide utilization is able to provide an economic incentive to offset the cost of carbon dioxide capture. Therefore, the opportunities of carbon dioxide capture and utilization are focused on in this work.

1.2.1 Carbon dioxide capture

In carbon capture, separation processes are used to remove the carbon dioxide from the rest of the gas stream, whether these are flue gas streams or natural gas streams for the pipeline. There are three types of carbon capture: (i) pre-combustion capture, (ii) oxy-fuel combustion, and (iii) post-combustion capture (Wilcox, 2012). These three and the types of separation processes that can be implemented for each are shown in Figure 1.1 (Wilcox, 2012).

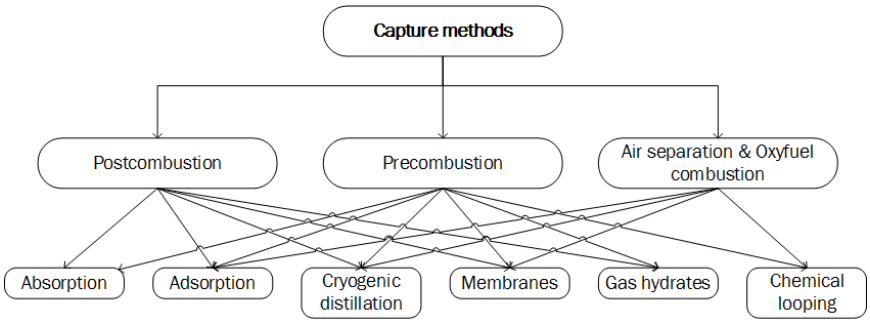

Figure 1.1. Different types of capture processes according to the types of capture.

Oxy-fuel and pre-combustion capture alter the process to reduce emissions formed. However, post-combustion capture removes the emissions after they have been

formed and is therefore applicable to the largest range of stationary emission sources. In addition, post-combustion capture results in a purified carbon dioxide stream that can be utilized or stored. As a result, post-combustion capture is considered in this work. Post-combustion capture processes are defined according to the separation mechanism involved (IPCC, 2005):

1. Adsorption: use of a solid compound to form a complex with the compound to be removed, thereby transferring it to the solid phase.

2. Membrane Separation: use of a driving force (the difference in the concentration or partial pressure between the two ends of the membrane) to filter the mixture selectively using particle size or other interactions with the membrane.

3. Absorption: use of a solvent to cause transfer of a compound from one phase into another; more specifically, uses mass transfer to transfer a compound between gas and liquid phases.

4. Other: there are other methods which are also investigated but not with as much interest as the other methods. This includes cryogenic separation methods and pressure swing separation.

1.2.1.1 State-of-the-art

Carbon capture is necessary in order to remove carbon dioxide from emissions into the atmosphere to reduce the concentration and thereby reduce the threat of global warming. Research has been devoted to the development of all types of post-combustion capture technologies. Research is focused on developing carbon dioxide capture processes that are economically and environmentally sustainable by all mechanisms described.

Absorption/Desorption processes are the predominantely considered methods of removing carbon dioxide from flue gas/off-gas streams (Wilcox, 2012). Absorption processes use solvents to remove the carbon dioxide from a gas. Physical absorption relies on the solubility of the carbon dioxide in the solvent. Meanwhile, reactive absorption also relies of the reactivity of the carbon dioxide and the binding component. Reactive absorption is often required to overcome the low solubility of carbon dioxide and the slow absorption (Wilcox, 2012). Research is focused on the development of suitable solvents which provide a high solubility, rapid diffusion and a good binding agent. Amines are the dominant class of solvents in reactive absorption, of which monoethyl amine (MEA) has been studied in the most detail (Wilcox, 2012). This is a result of its properties as a strong absorbant of carbon

dioxide, which means that the carbon dioxide can be absorbed in large amounts using less solvent. However, the downside to this strong absorption is the difficult desorption. Recovery of the absorbed carbon dioxide requires large amounts of energy, which is costly and not sustainable. Therefore, the primary research is focused on finding more sustainable alternatives with similar performance. For example, Gaspar et al. (2016) discuss the use of enzymes to enhance the capture using other solvent bases. They find that the capture is possible and requires less energy. However, the development of process technology that can enable the use of such enzymes effectively is needed. Ionic liquids are able to achieve high physical absorption rates due to the unique nature of the cation-anion interactions. Hasib-ur-Rahman et al. (2010) discuss the "tunable" properties that ionic liquids have making them promising for carbon capture processes. Ionic liquids for carbon capture can be designed to capture the desired compounds and facilitate an energy efficient desorption process. Therefore, research covers the development of optimal ionic liquids and industrial scale implementation of such processes.

Membrane processes are also studied to find capture membranes that are selective enough for implementation in carbon capture processes. However, the issue with membrane processes is the large volumes that need to be processed. Flue gases have low concentrations, but are in the largest amounts (IPCC, 2014). Therefore, these large flows need to be captured. However, for membrane processes, this then requires large pressure drops and large material costs. Khalilpour et al. (2015) study different materials and membranes for implementation, which is important to develop materials that are economic and effective.

There is also limited research in adsorption, amongst other capture technologies, and the selection of the proper adsorption agent (Hasan et al., 2012a). These technologies are not as promising as they often require large amounts of energy for the pressure changes or cooling to low temperature.

Depending on the emission source, the capture technology that is optimal may vary. Hasan et al. (2015) use superstructure optimization to evaluate the capture technology for different emission sources. They determine that depending on the source of the emissions, there is a more or less optimal capture technology. Of the four types of capture considered, the ideal, especially for the large quantity of low purity emissions from power plants, is absorption with monoethyl amine (MEA) (Hasan et al., 2015). However, for all the cases considered in this work, the carbon dioxide is purified (aka captured) to high purity (99.9% CO_2). Depending on the subsequent use, this high purity is not necessary. The different purity of captured carbon dioxide is considered in the work of Fjellerup (2015). The capture processes is optimized for a reduced carbon dioxide concentration at the outlet. In this way,

the reboiler duty, and consequently energy and cost, is greatly reduced to make the capture process sustainable. Additionally, the integration of the capture and conversion processes is performed. The concentration of the carbon dioxide that is captured needs to be evaluated. As carbon capture is a way of concentrating the carbon dioxide so that it can be used or stored, the concentration depends on the subsequent implementation. Therefore, more work needs to be done optimizing the concentration of the product concentration for the integrated CCU or CCS processes.

According to Styring et al. (2011), in their assessment of the status of the technology, there are differences in the maturity. Capture has been implemented in select industries for a while, especially in the gas processing industry. The most mature, and that which is industrially implemented to date, is absorption with monoethyl amine (MEA) (Styring et al., 2011). The high energy requirement and resulting cost negatively impacts the process. The cost is currently too high for such processes to make it promising, generally increasing power generation costs by at least 10% (von der Assen et al., 2013). The current carbon capture and storage (CCS) projects are listed in a database by the Global CCS Institute. There are a handful of test facilities for carbon capture globally implementing MEA capture processes. These are primarily in Norway and North America. With improvements in technology, these could spread to more industrial implementations. There is only one industrial implementation at commercial scale and that is the Boundary Dam Project by Sask Power in Canada (Armstrong and Styring, 2015).

1.2.2 Carbon dioxide utilization

Carbon dioxide utilization encompasses various reuses which are shown in Figure 1.2 (Aresta and Dibenedetto, 2007; North and Styring, 2015; Styring et al., 2011; Song, 2002).

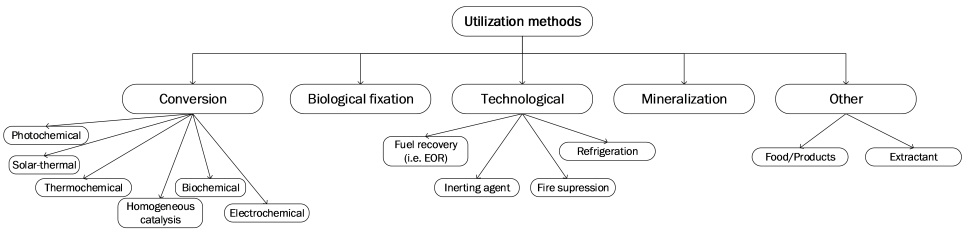

Figure 1.2. Different types of utilization processes

Some of these methods, use the carbon dioxide in the molecular form as the product. In these cases, the carbon dioxide is only relocated from the atmosphere

to other purposes, such as in fire extinguishers or the use in enhanced oil recovery. In mineralization, biological fixation and conversion, the carbon dioxide is transformed to another product. Conversion is the use of a reaction, chemical or biochemical, which uses the carbon dioxide as a reactant to produce value-added products. While all these utilization alternatives can play a valuable role, this work will focus on conversion. Chemical and biochemical conversion present potential as they have the possibility of finding alternative processes to produce products currently used industrially in a large scale, including fuel replacements, and are therefore a dominant research focus. In addition, conversion can result in net negative carbon dioxide emissions, where more carbon dioxide is consumed than is emitted. Due to the chemical stability of carbon dioxide (Aresta et al., 2013), the feasible and sustainable processes and products are limited. The products that can be produced often require an energy carrying co-reactant, such as hydrogen.

1.2.2.1 State-of-the-art

The research is focused on developing new and better catalysts to increase the selectivity and conversion of processes to value-added products. The difficulty in chemical conversion is the amount of energy that is required to react carbon dioxide due to its chemical state (Aresta et al., 2013). Currently, promising research is being performed on improving catalysts to the reaction to alcohols, such as methanol, and acids, such as formic acid, amongst others. There is also the technological aspect that is investigated. This includes intensified reactor technology to overcome certain equilibrium limitations, such as membrane reactors in dimethyl carbonate production (Kuenen et al., 2016b). This is especially relevant for thermochemical conversion processes. Alternatively, there is another branch of research focused on electrochemical utilization reaction. This research is working on innovative ways of supplying the required energy.

Biological conversion processes are primarily focused on the development of algal processes to produce biofuels using carbon dioxide. These are promising and have been piloted by companies such as Shell (Styring et al., 2011). However, the technology is limited by the space required to grow the algae to produce the products efficiently. Therefore, research is focused on the development of algae that can grow in unique environments and the processes to contain it.

Carbonylation is a promising option as a long-term storage option that can utilize the carbon dioxide in rocks and other construction materials (IPCC, 2005). Carbonylation research is focused on accelerating the process sustainably (Styring et al., 2011). This uses pressure and pretreatment of materials. However, with exothermic reactions and the energy required to accelerate the process, this is

difficult. Therefore, research is dedicated to resolving these issues.

Carbon dioxide conversion is mature in certain areas, such as urea production (Styring et al., 2011). In addition, there is a methanol production process in Iceland from Carbon Recycling International (Carbon Recycling International (CRI), 2017). However, other than the previously implemented conversion processes (primarily urea), only methanol has been considered industrially. Pilot processes to other products have been developed, such as the production of a polymer in the DREAM project (Styring et al., 2011). Hopefully, with new catalysts and process innovations, this number will increase.

1.2.3 Combined carbon capture and utilization (CCU)

It is also important to consider the integrated capture and utilization processes. Little research focuses on this. By looking at the combined system, it is possible to consider not only the individual processes, but also the interactions between them. Frauzem (2014) considers a CO_2 hydrogenation-based methanol plant integrated with a carbon dioxide capture plant employing the monoethanolamine (MEA) solvent with a reduced purity carbon dioxide stream. By considering the concentration of the captured stream, it is possible to optimize the combined process to reduce the overall energy. Additionally, the optimization of the supply chain, in terms of location of capture and utilization or storage facilities and the types of utilization or storage needs to be considered. Hasan et al. (2014) developed a large-scale (nationwide, regional, and statewide) CCUS network model and determined an optimal solution that minimizes the cost to reduce stationary carbon dioxide emissions in the United States. More than 3,000 emission points and various alternatives of carbon dioxide capture technologies (absorption, adsorption, and membrane-based), utilization (enhanced oil recovery) and sequestration (in saline formations and un-mineable coal bed areas) are considered in this study. There are some pilot scale facilities involved in capture and utilization. However, none of them have considered the integrated effects of the processes on each other. Rather, they have been developed and optimized individually.

1.3 Objective of the PhD project

As the environmental concerns grow regarding the amount of carbon dioxide emissions, methods of reducing emissions to the atmosphere need to be developed. In order to do this, a combination of improved energy efficiency of processes and carbon dioxide capture, storage and/or utilization is needed. Of these, carbon dioxide capture and utilization, especially conversion, is promising as it provides

economic incentive, easy implementation in current infrastructure, and the potential to be a net reduction of carbon dioxide emissions. However, in order to address the environmental concerns, the sustainable design of carbon dioxide capture and utilization processes needs to be ensured. To realize this, the objective of this work is the development of a framework for the sustainable design of carbon dioxide capture and conversion processes. This framework incorporates computer-aided methods and tools for the synthesis, design and intensification of sustainable processes. This framework is then applied to the development of sustainable carbon dioxide capture and conversion processes considering different scenarios. In addition to the sustainable design of these processes, these scenarios provide insight into the areas that these processes have the most potential. Through the use of the framework, sustainable capture and conversion processes can be achieved, which produce value-added chemicals and are net carbon dioxide reducing.

1.4 Structure of the PhD thesis

This thesis contains the following chapters:

1. Introduction: The first chapter of this thesis is dedicated to introducing the motivation for the PhD, the objective of the project, and structure of the thesis.

2. Literature review: In this second chapter, the necessary literature is reviewed to understand the existing methods and tools and determine the gaps that need to be filled by this work and future work. In addition, this review provides the foundation for the development of the framework.

3. Framework: Thirdly, the developed framework is presented in it's entirety. This includes the workflow and data flow, developed methods and tools and additional methods and tools incorporated into the framework.

4. Application: The application of the framework to various case studies is detailed in the fourth chapter. These case studies consider various scenarios for a complete understanding of the application. The results are then discussed for each of the case studies in this chapter.

5. Perspectives: Some perspectives on the role and potential of carbon dioxide capture and utilization processes are presented in the fifth chapter.

6. Conclusion: Finally, the sixth chapter offers some conclusions on the PhD work, including the objectives and gaps addressed as well as future work that still needs to be performed.

Chapter 2

Literature Review

Summary and significance:

In this chapter, the relevant literature is reviewed. This literature provides the necessary information to develop an understanding of the elements needed for the development of a framework for the sustainable design of carbon dioxide capture and conversion processes. In order to sustainably design these processes, the concepts of process synthesis, process design, process intensification, and sustainability are reviewed. In addition, the application of these concepts to carbon dioxide capture and conversion is stated. A framework also requires a data storage system and therefore concepts related to ontologies are also presented. Finally, the gaps in the existing literature are discussed and the areas that this work attempts to fill are pointed out.

Outline:

The sustainable design of carbon dioxide capture and utilization processes encompasses the reaction, the synthesis of the processing route, the design of the process, innovation (inclusive of process intensification), ontologies to organize all the information and data, and sustainability analysis. A framework is an architecture which provides the steps along with the necessary inputs and the resulting outputs, to achieve the desired goal. Each of these elements needs to be well understood in order to develop a framework for the sustainable design of carbon dioxide capture and utilization processes. In this chapter, all the relevant areas for developing and implementing a framework for the sustainable design of carbon dioxide capture and utilization processes are covered. First, the design problem and the methods for the different elements of this overall design problem are described thoroughly, from synthesis to design to intensification. Then, how to generate the reactions will also be described as this is especially important for carbon dioxide conversion processes. In addition, how to assess the sustainability of the processes at all levels of design needs to be understood. These elements are reviewed in general and then the specifics are applied to carbon dioxide capture and utilization processes. All the elements of setting up a framework to address the design of such processes require data. Therefore, how to systematically organize such data in ontologies is discussed. This review of available literature serves to provide a background and understanding of all the elements needed in the development of a framework for the sustainable design of carbon dioxide capture and utilization, especially conversion, processes. Subsequently the gaps and the role of this work in addressing these are stated.

2.1 The overall design problem

The overall process design problem involves determining how to produce a product from a given raw material or materials. This design problem can be described as a mathematical programming problem. The objective of the design problem is to find the optimal, according to the objective function, sequence of operations to convert (transform via chemical reaction or other operation) raw material to product, including the design of the equipment. The generic form of this problem is described by Equations 2.1 - 2.5 (Duran and Grossmann, 1986).

$$F_{obj} = \min / \max_{x,y} Z = C^T y + f(x) \tag{2.1}$$

s.t.

$$r(x) = 0 \tag{2.2}$$

$$s(x) + B(y) \leq 0 \tag{2.3}$$

$$x \in R^n \tag{2.4}$$

$$y(0,1)^l \tag{2.5}$$

In this definition, the objective function, F_{obj} is a function of the continuous variables, x, and discrete variables, y. The continuous variables are related to processing information, including flow rates, design parameters and so on, while discrete variables are related to decisions, including those related to topology (the arrangement, including sequence, of the intervals, aka units or tasks). C^T is a matrix of cost coefficients related to the discrete variables. $f(x)$ is the cost related to the continuous variables. The objective function is subject to linear, $r(x) = 0$, and non-linear, $s(x) + B(y) \leq 0$, constraints. These equations yield a mixed-integer (non)-linear programming problem (MI(N)LP). Whether or not it contains non-linearities determines whether it is an MINLP or MILP.

There are different types and levels of problems that can be described by this formulation. This general formulation can, more specifically, be applied to process synthesis and process intensification, which are discussed in more detail in Section 2.1.1 and 2.1.2. Within these sections, important methods and tools will be summarized. The application of process synthesis and process intensification in the area of carbon dioxide capture and utilization are presented in Sections 2.4.1 and 2.4.2, respectively.

2.1.1 Process synthesis

The process synthesis problem is defined as: given a raw material, or set of raw materials, and a product, or set of products, determine the optimal configuration, including sequence and equipment, to achieve the objective. This encompasses the synthesis of different elements of processes, from heat exchanger networks to reactor networks to separation sequences, all the way to entire processes. For this work, focus is placed on the synthesis methods for entire processes, as these are applied to the synthesis of carbon dioxide capture and utilization processes in their entirety. Methods for addressing problems for all these areas can be split into: (i) heuristic, (ii) mathematical programming, and (iii) hybrid methods.

2.1.1.1 Heuristic

Heuristic (rule-based) and knowledge-based methods are defined as methods which implement a set of rules, often based on collected know-how and expert knowledge, in a systematic manner to solve the synthesis problem. Heuristic methods are advantageous because of their ease of use and ability to quickly provide solutions. However, these methods do not always provide the optimal solution (not

all the alternatives are necessarily considered and the global optimization cannot be guarenteed) and the rules can be contradictory (i.e. first separate the most prevalent compound and perform the easiest separation first are two heuristics that can be difficult to implement if they conflict when the easiest separation is the least prevalent compound and so on). The methods for heuristics of entire chemical processes are limited. Douglas (1985) developed an extremely important method for the synthesis-design of chemical processes. It follows the initial work by Siirola et al. (1971), Nath and Motard (1981) and Lu and Motard (1985) in the synthesis of entire chemical processes. Siirola et al. (1971) first introduced the use of computers to automate heuristic methods, first for separation sequences and later for entire chemical processes (Siirola, 1996). Additionally, Nath and Motard (1981) expanded this method to incorporate two phases: a heuristic method for an initial structure and then an evolutionary method to change the structure successively. This work was expanded to cover entire flowsheets (Lu and Motard, 1985).

Douglas (1985) provides the first introduction into the hierarchical approach to process synthesis. This method decomposes the design problem into various levels, a hierarchy of decisions. In order to utilize the method, the user must follow these levels in order, implementing the heuristics for each level. There are five levels in the method: (i) batch vs continuous, (ii) input-output structure, (iii) recycle structure and reactor considerations, (iv) separation system specification (split into vapor recovery and liquid recovery), and (v) heat exchanger network. This hierarchical method introduces hierarchical decision making in process synthesis and provides an easy method for the design of entire chemical processes with heuristics. This method provides the foundation for all further heuristic methods for the design of entire chemical processes.

Methods that employ chemical engineering, by the way of thermodynamics, try to include a justifiable reason for the steps that are followed for the synthesis methods utilizing thermodynamic laws and properties to calculate aspects of the synthesis; pure component and mixture properties are determined and these values are implemented through a series of equations or graphs. Jaksland et al. (1995) exploit the physical aspect of the different properties associated with different separation processes to synthesize separation sequences. Jaksland and Gani (1996) elaborate this work to consider entire processes. This hierarchical method incorporates two levels that are founded on thermodynamic-based algorithms. Following the steps involved, this method calls for the implementation of data and tools to understand the behavior of the system. Each step targets different elements of the separation task by applying various thermodynamic laws. Using a method similar to the CAMD (computer aided molecular design) problem, the sequences are formulated based

on properties indicative of certain behavior and then combined using combinatorial laws. The implementation of this method has been applied to two cases, which illustrate how this method can be used to design separation sequence alternatives containing the optimal solution.

As part of heuristic methods, there are graphical techniques relying on thermodynamic knowledge to get a basic understanding of the system and thereby design the process. Sempuga et al. (2010) and Fox et al. (2013) developed a graphical method for the synthesis of entire chemical processes. This method allows for the incorporation of heat and work into the design. This utilizes enthalpy and Gibb's free energy and represents them in the GH-space. With the visualization of the material, energy and work, it is possible to find the process that is as thermodynamically efficient as possible. The explanation of the graphical method is highlighted through the application to a simple and generalized chemical process as well as to Carnot cycles and reforming processes. With a thorough description of the elements of the graph, it is possible to use it for the design of entire process with thermodynamic considerations. The final flow sheet represents the thermodynamically ideal solution. This reveals that the GH-space is a way of allowing the user to interpret the thermodynamics and apply this in the design.

2.1.1.2 Mathematical programming

With the advances in computational power, it has also become possible to formulate and solve the mathematical optimization problems. However, it is still not always possible to solve the problems to global optimality due to their size (computationally intensive) and complexity. The synthesis of the entire process flowsheet can be performed through a superstructure optimization approach (Grossmann, 1990). A superstructure contains the alternative processing units and their connectivity, which is modeled by discrete or binary variables representing the choices of the unit that has potential to be selected in the final flowsheet. With the superstructure formulation, optimization techniques and solution strategies are needed and proposed to obtain optimal configurations in the process system.

Duran and Grossmann (1986) first developed an Outer-Approximation (OA) algorithm for solving Mixed Integer Non-linear Programming (MINLP), which was further improved by other researchers (Kocis and Grossmann, 1987, 1989; Turkay and Grossmann, 1998). This algorithm consists of two parts: (i) the optimization of the Non-linear Programming (NLP) sub-problem with the initial continuous variables for a specific flowsheet structure and (ii) optimization of the Mixed Integer Linear programming (MILP) master problem for generating new candidate flowsheet configurations in order to determine an optimal configuration. But,

this approach runs into limitations when addressing non-convex problems. Subsequently, Raman and Grossmann (1994) introduced the Generalized Disjunctive Programming (GDP) as an alternative representation of mixed integer programming. Kocis and Grossmann (1987, 1989) introduce the Modeling/Decomposition (M/D) strategy in order to solve the Outer Approximation with the Equality Relaxation (OA/ER) algorithm. This method separates the superstructure into nodes (process units) and their interconnections.

Frameworks have been developed relying on these solution methods; Papalexandri and Pistikopoulos (1996) present a general modeling framework for process flowsheet synthesis based on mass/heat principles; in retrofitting cases, Jackson and Grossmann (2002) offered an optimization strategy using a multiperiod generalized disjunctive programming (GDP) model for evaluating a complete process network at a high level and analyzing a detail process flowsheet at a low level. In order to allow simultaneous approach, Papoulias and Grossmann (1983a,b,c) proposed MILP programming for simultaneous synthesis of a total processing system by considering the interactions among three different subsystems: chemical plant, heat recovery network and utility plant. Duran and Grossmann (1986) developed a solution procedure for simultaneously handling heat exchanger networks and process networks. This method is based on a pinch method for the utility. A simultaneous optimization of water, heat and flowsheet was proposed by Yang and Grossmann (2013), where the upper bounds are determined using an LP targeting model.

Recently, Quaglia et al. (2012) proposed a systematic framework for the synthesis of processing networks by integrating business and engineering aspects. This framework proposes a generic processing interval model to represent the processing units requiring the definition of the parameters in the model. Thereby, the different alternatives are all described by the same model. The proposed framework is comprised of different methods and tools needed to define and formulate problem as a MINLP. This generic process interval model was adapted and modified from a previous study dealing with a bio-refinery processing network Zondervan et al. (2011) by adding a waste separation task in the process interval.

The described methods for entire flowsheet synthesis have been applied to various case studies. These include the synthesis of chemical processes (Lee and Grossmann, 2003) bio-refinery processes (Martín and Grossmann, 2013), wastewater treatment networks (Quaglia et al., 2014). An extensive review on MILP and MINLP techniques can be found in Grossmann (2002).

2.1.1.3 Hybrid

While both the aforementioned approaches have their advantages and disadvantages, it is possible to take advantages of both and avoid some of the disadvantages. This is achieved via hybrid methods. These methods concentrate on narrowing the search space in order to reduce the size of the synthesis problem and to obtain near-optimal solutions which deserve to be analyzed in more detail.

Lu and Motard (1985) propose a hybrid method to synthesize complete flowsheets, where first the preliminary process flowsheet is generated by using successive linear programming and then the separation techniques are synthesized using heuristics. Afterwards, further improvements are found using evolutionary principles. Similarly, Mészáros and Fonyó (1986) and Mizsey and Fonyo (1990) introduce a framework using hierarchical decomposition and mathematical optimization methods to generate and screen processes. These are then verified and solved using algorithmic methods. Hostrup et al. (2001) present a method based on thermodynamic insights and mathematical programming. This method consists of three main steps: (i) pre-analsyis, (ii) flowsheet and superstructure generation, and (iii) simulation and optimization. First, alternatives are generated with thermodynamic insights. Then, MINLP models are used to solve the optimization problem. Later, Li et al. (2003) use conflict-based analysis and mathematical programming to perform process synthesis with waste minimization. A three-step hierarchy is used to generate alternatives: (i) waste sources identified, (ii) improve characteristics with heuristics, and (iii) solve the MINLP optimization.

d'Anterroches and Gani (2005a,b) introduce a method for flowsheet synthesis based on the principles of the group-contribution. A framework for computer aided flowsheet design (CAFD) is presented, in which process flowsheets are synthesized in the same way as atoms or groups of atoms are synthesized to form molecules in computer aided molecular design (CAMD) techniques. In this framework, process-groups are used as building blocks, connectivity rules connect the process-groups, and different property models are used to compare the alternatives generated. These building blocks represent various process operations, the connectivity rules are heuristics and the alternatives are evaluated mathematically with the different property models. This framework is expanded to include different flowsheet property models by Tula et al. (2015) and was successfully applied to industrial important case studies involving chemical (Tula et al., 2015) and biochemical processes (Alvarado-Morales et al., 2010).

2.1.2 Process intensification

Process intensification involves the enhancement of the function of the process by performing one or more tasks simultaneously in a unit or in the design of a new unit operation. The overall design problem formulation described previously (Equations 2.1 - 2.5 in Section 2.1) also describes the process intensification problem. More specifically, the process intensification problem is: given raw materials and products, find a process route considering innovative techniques and equipment to improve the process by considering integration of unit operations, integration of functions, integration of phenomena and/or targeted enhancement of a phenomenon within an operation (Lutze et al., 2010). However, an extension of the unit operations search space is needed in order to include other types of unit operations not frequently considered during process synthesis, that is, hybrid (used interchangeably with intensified) unit operations. Therefore, the general definition of the process synthesis problem must be expanded in order to include constraints and performance criteria that provide the opportunity, where applicable, to consider hybrid/intensified unit operations when performing process synthesis. Similar to process synthesis methods, process intensification methods can be divided into the 3 categories: heuristic, mathematical programming and hybrid.

2.1.2.1 Heuristic

To date, there are no heuristic methods for the process intensification of entire processes. This is the result of the lack of experience with most intensified equipment. However, there are heuristic methods for the application of select intensified equipment, particularly reactive distillation and dividing wall columns. For reactive distillation, Bessling et al. (1997) introduce the concept of reactive distillation lines to study the feasibility of reactive distillation. In this work, a procedure for the identification of reactive distillation processes is developed using these lines and the reaction space concept. In addition, Barnicki et al. (2006) present heuristics for introducing reactive distillation in a process. Kiss et al. (2007) present a case study from Akzo Nobel Chemicals on integrated design of a reactive divided-wall column (RDWC). In this industrial example, two integrated units, reactive distillation and divided wall columns are combined to make a single, more intensified unit which improves the process.

2.1.2.2 Mathematical programming

Similar to heuristic methods, mathematical programming methods for process intensification of entire processes, have not been proposed. Rather, methods for

specific intensified equipment, such as reactive distillation, have been proposed. Ciric and Gu (1994) use a superstructure approach to synthesize reactive distillation columns. In this approach, a rigorous MINLP model is developed, which considers each tray individually and then optimizes the total annualized cost. Caballero and Grossmann (2004) present a superstructure optimization approach for the design of separation sequences for zeotropic mixtures. This procedure uses two stages, where, in the first, the sequence of tasks is selected and then, in the second, the configuration is determined. This approach considers conventional distillation as well as intensified alternatives in the superstructure optimization. Urselmann et al. (2011) present a memetic algorithm (MA) for the global optimization of design problems. In this way, the sub-problems are solved by mathematical programming solvers. This method is applied to the design of reactive distillation columns (RDC). Amte (2011) present work on reactive distillation-pervaporation (RD-PV) systems. In this work, the optimization of the hybrid system is done by formulating the problem as a superstructure and solving the MINLP formulation. In this work, they present the economic feasibility of such a hybrid process and the use of mathematical programming to solve the problem.

2.1.2.3 Hybrid

Alternatively, hybrid methods for the process intensification of entire processes and individual parts of the process have been applied.

Schembecker and Tlatlik (2003) propose a method that combines superstructure optimization and heuristics for systems containing reaction and separation. By considering the elements and the reactions that are involved, this method can be used to generate intensified units. Franke et al. (2008) propose a three stage method for the design of hybrid separation schemes. First, heuristics are used to generate alternatives; then, shortcut methods are used to optimize these alternatives; finally, MINLP optimization is used to rigorously optimize the most promising options. This method is applied to the design of a hybrid distillation/melt crystallization process. Marquardt et al. (2008) present a similar three stage framework for the design of separation flowsheets for multi-component mixtures that also consider hybrid and intensified options. First, the flowsheets are generated, then these are evaluated with shortcut models, and finally MINLP optimization is used to determine the optimal. Sun et al. (2009) develop a four step procedure specifically to deepen the mass integration for reactive distillation. This is then evaluated by application to four hypothetical systems. Errico et al. (2008) propose two retrofit alternatives for an industrial case study using thermal coupling. In the presented study this is able to significantly reduce the energy consumption. These methods,

however, do not extend beyond existing equipment.

Freund and Sundmacher (2008) introduce functional modules based on elementary process functions to describe chemical processes rather than unit operations. This allows for the identification of the areas in the process where intensification should be considered. Peschel et al. (2010) and Peschel et al. (2011) use this new description of chemical processes in the development of novel reactor networks using a three level approach. First, the optimal reaction route is found amongst a set of different alternatives. Second, mass and energy balances are incorporated into the optimization to design catalyst packing. Finally, technical constraints for the equipment are determined by finding the appropriate unit operation. This method is applied to two reactors.

Siirola (1996) presents a Means-Ends Analysis to identify tasks with the help of expert knowledge to satisfy process requirements. In this way, intensified equipment can be included via expert knowledge and then evaluated according to performance criteria. This method is then applied to the synthesis of an intensified solution using reactive distillation for the production of methyl-acetate.

Papalexandri and Pistikopoulos (1996) first introduce the phenomena scale for the synthesis of processes. They introduce the generalized modular (GMR) approach to represent the alternatives in a block-superstructure based on fundamental mass and heat transfer principles. In this way, it is possible to consider equipment outside of predefined or conventional unit operations. The presented framework involves the generation of the superstructure with the help of heuristics and engineering knowledge. Then, the superstructure can be optimized to find the process alternatives. This framework was applied to ethylene glycol production, resulting in the synthesis and design of a process using reactive distillation.

Rong et al. (2004) first introduce a seven step method for process intensification based on chemical phenomena to overcome thermodynamic limitations. The chemical phenomena represent key features of processes, including phases, flow patterns and operating modes. This method is extended by Rong et al. (2008) to a ten-step process. In both, these steps are split into three stages; where the first stage is the identification of the bottleneck of the process, the second stage is the identification of the phenomena and then the final stage is the generation of alternatives. This method is based on a trial-and-error approach where promising phenomena are manipulated to improve the design iteratively via seven principles. This method is highlighted in the application to the production of hydrogen peroxide and peracetic acid.

Arizmendi-Sánchez and Sharratt (2008) introduce a framework for phenomena-based process intensification based on the modularisation principles. In this work,

there are phenomena that represent the behavioral level consisting of accumulation, generation and transport of mass and energy, which are bounded by structural phenomena. These phenomena can be aggregated sequentially to form tasks and then processes. Modularisation criteria are then used to ensure that consistent qualitative and quantitative models are generated. This framework is applied to a theoretical example of a process containing two competing reactions.

Lutze et al. (2013) propose an innovative and systematic computer-aided methodology to perform synthesis-design at the phenomena scale for the intensification of the entire process. This method was further expanded by Babi et al. (2015). By describing the process with phenomena rather than unit operations, the search space can be expanded to include innovative and hybrid technologies. This hybrid method uses phenomena to describe the process; predefined rules, analogous to computer aided molecular design (CAMD), are used to combine phenomena building blocks (PBBs) to simultaneous phenomena building blocks (SPBs) which can describe any process. These SPBs or sets of SPBs are then linked to describe an entire process, which is then evaluated to find innovative and intensified alternatives. This method has been applied to the intensification of dimethyl carbonate (DMC) production (Babi et al., 2016; Kongpanna et al., 2016).

2.2 Reaction path synthesis

The synthesis, analysis and evolution of reactions is the goal of reaction path synthesis, which is an important part of chemical and biochemical process design (Powers and Jones, 1973; Govind and Powers, 1981; Nishida et al., 1981; Barnicki and Siirola, 2004; Klatt and Marquardt, 2009). The problem of reaction path synthesis is defined as follows: given a set of desired product(s) or starting raw material(s), determine the best (optimal) reaction path that utilizes the given raw material or produces the desired product(s), while maximizing/minimizing a pre-defined objective function subject to constraints. Reaction path synthesis has been extensively discussed by Wipke (1974a,b); Wipke and Dyott (1974) and Wipke and Howe (1977). The problem can be split into two tasks: (i) generation of reaction paths and (ii) evaluation of the alternatives to determine the alternatives. Methods have been developed to address this problem and they can be classified in two categories: synthetic (determining products from given raw materials) and retrosynthetic, or antithetic (determining raw materials from given products) (Powers and Jones, 1973; Nishida et al., 1981). Within these synthetic and retrosynthetic methods, the generation of alternatives is performed in three ways (Agnihotri and Motard, 1980; Nishida et al., 1981)

1. Logic centered, also known as logic-based: In these methods, intermediates are generated iteratively to form a tree of molecules. These methods use parameters or mathematical representations to synthesize molecules and reactions.

2. Information-based or rule-based, direct associative: These methods use structural sub-units combined with certain reactions to produce target molecules. All this information on sub-units and transforms (reactions or chemical transformations to produce target molecules) is stored in a database or library.

3. Hybrid methods: These methods combine elements of different types of methods, such as heuristics and mathematical optimization.

2.2.1 Logic-based methods

The first to identify an underlying mathematical model for the representation and generation of chemical molecules was Ugi and co-workers (Ugi and Gillespie, 1971; Ugi et al., 1972; Dugundji and Ugi, 1973; Blair et al., 1974; Gasteiger et al., 1974) via a synthetic approach. In this work, a molecule is represented by a Bond-Electron (BE) matrix and the collection of such matrices forms an EM (ensemble of molecules) matrix. The reactions then change the BE matrices to show the new electron-bonding. This representation of molecules is used by Agnihotri (1978) in the program CHIRP.

Hendrickson (1971, 1975a,b) presents a method in which the molecule is represented by parameters for the types of atoms and the topological structure of the bonds. Then, during a reaction, the molecule is transformed to another state by changing the parameters in various ways.

Subsequently, Rotstein et al. (1982) present a framework in which reaction paths are synthesized based on algebraic properties of reactions in the so-called ΔG-T space. In this work, they use retrosynthesis to find reactions from a set of raw materials to a fixed product with various byproducts. In the method, the ΔG-T space is manipulated algebraically to generate reaction paths which can then be screened thermodynamically. Heuristic thermodynamic screening was introduced by Govind and Powers (1977), Agnihotri and Motard (1980) and Rudd (1976), in which rules based on ΔG and other thermodynamic properties are used to screen the reactions.

2.2.2 Information-based methods

Corey and Wipke (1969) first developed a methodology for retrosynthesis, which was then implemented in a computer system OCSS (Organic Chemical Simula-

tion and Synthesis). In this methodology, a connection table is used to represent the molecules and these connection tables are then transformed to change the molecules and determine reaction paths. Subsequently, the computer program LHASA (Logic and Heuristics Applied to Synthetic Analysis) was developed by Corey (1971) and Corey et al. (1972). This is similar to the previous computer system, but now incorporates man-computer interaction. This computer program also uses a retrosynthetic approach to generate all precursors to a certain compound using heuristics and logic. Wipke (1974a,b), Wipke and Dyott (1974) and Wipke and Howe (1977) generate the program SECS (Simulation and Evaluation of Chemical Synthesis), which is based on LHASA. Govind and Powers (1981) developed the program REACT for the retrosynthetic reaction path synthesis from a chemical engineering perspective. This program searches a databases of reactions to transform the molecules which are represented by a linear list of numbers.

Gasteiger et al. (1990) and Gasteiger et al. (2000) present three systems: EROS (Elaboration of Reactions for Organic Synthesis), WODCA (Workbench for the Organization of Data for Chemical Applications) and CORA (Classification of Organic Reactions for Applications). EROS uses electronic and energy effects to model the reactions and predict the products. WODCA is used to plan the synthesis of combinatorial libraries. CORA is used to analyze all the reactions found in databases to obtain the necessary information for the design and simulation of chemical reactions. Crabtree and El-Halwagi (1994) introduce a hierarchical approach to incorporate environmental criteria in the generation. In this work, the goal is to produce environmentally acceptable reactions (EARs) by increasing the complexity as the number of alternatives decreases. Thereby only performing a detailed analysis of the most promising reactions.

2.2.3 Hybrid methods

Hybrid methods use different aspects of the information-based and logic-based methods to take full advantage of the information and methods available. Funatsu and Sasaki (1988) developed the program AIPHOS (Artificial Intelligience for Planning and Handling Organic Synthesis) for the generation of possible precursors for a product, by combining the logic-based elements in the form of a central algorithm and information-based elements in the form of a database.

Buxton et al. (1997) decompose the synthesis problem into a series of steps in order to include environmental impact minimization. First, computer-aided molecular design methods, taken from Gani et al. (1991) and amended by Constantinou et al. (1996), are used to design the raw material and co-products, then promising candidates are selected using logic-based methods, and finally MEIM (Methodology

for Environmental Impact Minimization) (Pistikopoulos et al., 1994) is used to evaluate the resulting mechanisms in detail.

Li et al. (2000a,b) introduce a systematic method to ensure sustainability by reducing avoidable pollution. In this method, simple stoichiometric reactions (SSRs) are used to represent the different steps in the network. Then, optimization is used to identify promising reactions. Similarly, Hu et al. (2004) extend this method for waste minimization. In this work, mathematical transformations are used to generate the reactions from simple stoichiometric reations. Then, the optimization is performed at two levels: (i) an economic evaluation of the overall reactions and (ii) decomposition of the overall reactions to find the optimal (in terms of thermodynamic feasibility) set of sub-reactions.

There are also alternative methods based on metabolic pathway analysis. Voll and Marquardt (2011) first propose metabolic analysis methods by combining two approaches: (i) computer-aided molecular design (CAMD), to find promising targets, and (ii) reaction network flux analysis (RNFA), to identify and screen the different alternative routes.

2.3 Sustainability

Sustainable development is generally defined according to the Brundtland report as development without compromising the ability of future generations to meet their needs (Hueting, 1990). In process design, sustainability is incorporated by considering alternative and renewable feedstocks (biomass and carbon dioxide), alternative energy sources (solar and wind), and improving the efficiency of processes (Jayal et al., 2010). Sustainability can also be defined by certain metrics, as defined by Institution of Chemical Engineers (IChemE) (2002). Here sustainability is defined according to various process parameters, split into economic, environmental and social metrics.

In order to measure the sustainability, there are various methods of determining sustainability. One of the effective methods is lifecycle assessment (LCA), which is to quantify the potential environmental impacts throughout the chemical product or process lifecycle (cradle-to-cave). Using this method, one can evaluate improvement options to identify the more sustainable designs (Kalakul et al., 2014). For this, useful software exists, including Ecoinvent (Ecoinvent, 2016), SimSci (SimSci, 2016), SustainPro (Carvalho et al., 2013), and LCSoft (Kalakul et al., 2014), which provide various analysis-assessment options with massive databases.

Carbon footprint is especially important for carbon dioxide utilizing processes. By reducing the amount of carbon dioxide, one element of sustainability can be

achieved. However, in order to achieve non-trade-off solutions, the other metrics (global warming potential (GWP), OPEX, CAPEX, etc.) also need to be evaluated.

2.4 Process Systems Engineering (PSE) issues in CCU

Over the past two decades, carbon dioxide capture and utilization (CCU) processes have been receiving increasing attention due to their potential to help reduce the amount of carbon dioxide in the atmosphere by taking emissions and making further use of them. CCU has been the topic of an increasing number of papers covering a variety of elements of CCU. These papers review the details of reactions, new catalysts, information on developed technologies and the industrial status of such processes, together with life cycle impacts. A time line diagram showing the developments and the corresponding category of the topics is given in Figure 2.1.

As highlighted in Figure 2.1, there has been increasing research interest in topics related to CCU, thereby increasing visibility of it and promoting the possibility it presents in the abatement of carbon dioxide emissions.

2.4.1 Carbon dioxide utilization process synthesis and design

The general process synthesis problem can be more specifically defined for carbon dioxide conversion as: given carbon dioxide feedstock (either as flue gas or in a purer form from a carbon dioxide capture process), determine the optimal processing route to produce the desired product(s). For carbon dioxide conversion processes, as the amount of information related to reactions and processes is large, there is a need to determine the optimal amongst a large set of alternatives.

For carbon dioxide conversion processes, Prasertsri et al. (2016) use logic to screen the alternatives for the production of dimethyl ether (DME) from carbon dioxide. The most promising candidates from this screening step are then retained for further examination. In this work, three routes for the production of dimethyl ether utilizing carbon dioxide are taken for more rigorous design. Similarly, Roh et al. (2016b) use logic to screen amongst alternatives for the synthesis of methanol from carbon dioxide. In this case, the processing routes via direct hydrogenation and via syngas from bi-reforming are selected for further consideration.

Alternatively, mathematical programming and hybrid methods are recently growing in application. Especially the use of superstructures, is of interest. This involves the representation of the processing alternatives, linking raw materials and products, as a superstructure. Agarwal et al. (2009, 2010) used superstructure optimization to determine the optimal configuration of pressure swing adsorption processes for carbon dioxide capture. Similarly, Hasan et al. (2012a,b) used superstructure

	Reaction network generation	Processing route generation	Process design (without sustainability analysis)	Sustainability analysis (without process design)	Sustainable process design	Integration with other systems
Aresta and Galatola (1999)				X		
Teuner et al. (2001)					X	
Aresta et al. (2002)				X		
Indala (2004)			X			X
Xu et al. (2005)						X
Cho et al. (2009)			X			
Minutillo and Perna (2009)			X			X
Minutillo and Perna (2010)			X			X
Aboosadi (2011)			X			
Han and Lee (2011)						X
Jone et al. (2011)					X	X
Li et al. (2011)			X			
Lim et al. (2012)					X	
Taghdisian et al. (2012)					X	
Van-Dal and Bouallou (2013)			X			
von der Assen et al. (2013)				X		
Zhang et al. (2013)			X			
ADEME (2014)				X		
Hasan et al. (2014)						X
Cañete et al. (2014)			X			
Cignitti (2014)	X					
Luyben (2014)			X			
Park et al. (2014)			X			
von der Assen and Bardow (2014)				X		
von der Assen et al. (2014)				X		
Armstrong and Styring (2015)				X		
Babi et al. (2015)					X	
Dimitriou et al. (2015)			X			
Fjellerup (2015)					X	
Frauzem et al. (2015a)					X	X
Frauzem et al. (2015b)					X	
Kongpanna et al. (2015)		X			X	
Nguyen (2015)					X	X
Noureldin et al. (2015)			X			
Roh et al. (2015)					X	X
Taghdisian et al. (2015)					X	
Bertran et al. (2016)		X				
Kiss et al. (2016)			X			
Kongpanna et al. (2016)		X			X	
Martín and Grossmann (2016)						X
Pérez-Fortes et al. (2016)					X	
Prasertsri et al. (2016)		X			X	
Roh et al. (2016a)	X	X			X	X
Roh et al. (2016b)					X	

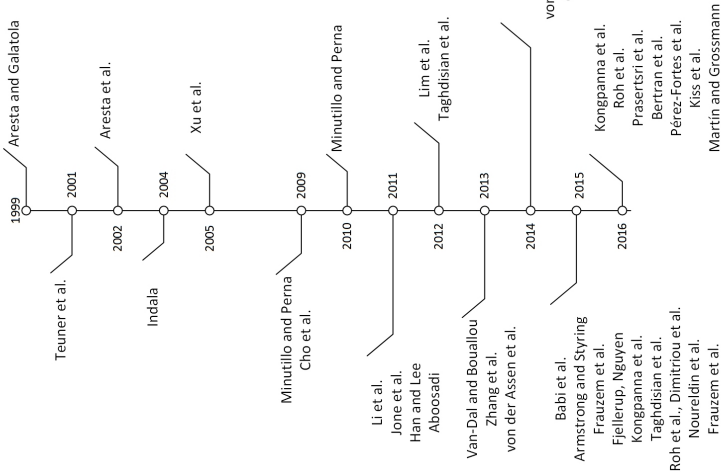

Figure 2.1. Time line of the research in CCU and the areas in which they focus (Roh et al., 2016a).

optimization to determine the carbon dioxide capture process for different emission sources.

In addition, Quaglia et al. (2012, 2015) introduce a generic model for the superstructure representation. In this model, the superstructure is broken down into processing steps containing processing intervals. These intervals have a generic model to describe the tasks being performed (mixing, reaction, separation). In the work of Kongpanna et al. (2015, 2016) this generic model is used in the superstructure optimization to determine the optimal production route for dimethyl carbonate (DMC) from carbon dioxide. This generic model has been modified by Bertran et al. (2016) and applied to a network of carbon dioxide conversion processes. In this work, the carbon dioxide conversion to three products with various routes are compared. This is represented by the superstructure in Figure 2.2. In addition, a software tool called Super-O (Bertran et al., 2015) is presented and implemented for the superstructure optimization; the use of the generic model is facilitated by the software tool to compare the production of three products from captured carbon dioxide.

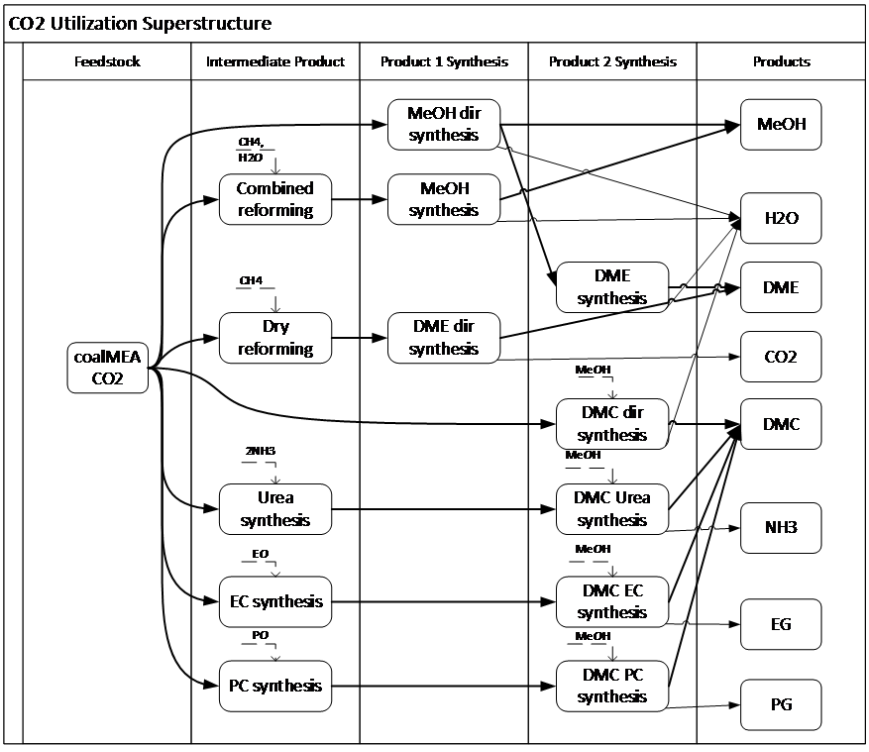

Figure 2.2. The superstructure representation of the network of methanol, dimethyl ether and dimethyl carbonate production processes from carbon dioxide (Bertran et al., 2016).

Given a processing route connecting feedstocks to target products, rigorous process design is performed to evaluate its economics and sustainability. For carbon dioxide conversion, process design is an essential step to go forward into more rigorous evaluation, improvement, and large-scale implementation. Even though most carbon dioxide conversions are at early stages of technical maturity, it is nevertheless important to determine their potentials early on, so that limited R&D resources can be directed to the most promising ones. In doing so, the entire process may be considered to understand the influence of all aspects of the process (North and Styring, 2015).

Process design methods and tools have been frequently applied in the study of carbon dioxide conversion to specific products. Table 2.1 lists recent publications that address process design for carbon dioxide conversion. It is noted that all of the studies targeted bulk chemicals as products. Methanol is the most popular product followed by syngas and dimethyl carbonate.

2.4.2 Process intensification in carbon dioxide utilization

Process intensification methods have not been greatly applied to carbon dioxide capture and utilization processes. While intensified processes are considered in some cases, these are incorporated on a case-by-case basis. Babi et al. (2015) and Kongpanna et al. (2016) apply methods of phenomena-based process intensification (Babi et al., 2014b,a, 2015) to design processes with intensified equipment; the use of intensified equipment, such as dividing-wall columns or membrane reactors, improves both the economics and sustainability compared to the base case design.

2.4.3 Carbon dioxide conversion reaction networks

Carbon dioxide is a stable molecule that is in an energetic potential well (Aresta and Dibenedetto, 2007) and, as a result, the reactions involving carbon dioxide as a reactant need to be carefully evaluated before considering associated processing routes. It is possible to generate and screen reactions which show promise and produce products that are of interest. The generation of reaction networks and the selection of the optimal reaction path, or reaction path synthesis, is an important step in synthesis and design of carbon dioxide conversion processes.

Following a heuristic approach, Aresta (2010); Aresta et al. (2016) and Otto et al. (2015) have collected information and compiled lists of reactions involving carbon dioxide as a reactant. In these compilations, the chemistry, detailed reaction information, catalysts available and operating conditions for various carbon dioxide conversion reactions are provided. Also, Centi et al. (2013) provide perspectives

Table 2.1. Selected list of published carbon dioxide conversion processes stating the product produced and whether sustainability is considered (Roh et al., 2016a).

Publication	Methanol	Syngas	DMC	Other	Sustainability?
Indala (2004)	X	X	X	Ethanol, DME, etc.	N
Minutillo and Perna (2010)	X				N
Taghdisian et al. (2012, 2015)	X				Y
Van-Dal and Bouallou (2013)	X				Y
Zhang et al. (2013)	X				N
Cañete et al. (2014)	X				N
Park et al. (2014)	X				N
Roh et al. (2015, 2016b,c)	X				Y
Frauzem (2014)	X		X		Y
Frauzem et al. (2015)	X		X		Y
Fjellerup (2015)	X			Formic acid	Y
Nguyen (2015)	X				Y
Pérez-Fortes et al. (2016)	X				Y
Kiss et al. (2016a,b)	X				N
Cho et al. (2009)		X			N
Aboosadi et al. (2011)		X			N
Lim et al. (2012)		X			Y
Luyben (2014)		X			N
Babi et al. (2015)			X		Y
Kongpanna et al. (2015, 2016)			X		Y
Li et al. (2011)				Methanol, DMC, DME together	N
Dimitriou et al. (2015)				Liquid fuel	N
Noureldin et al. (2015)				Mixed alcohol	N
Prasertsri et al. (2016)				DME	Y

on the chemical aspects of catalytic carbon dioxide conversion reactions that are relevant in determining new catalysts and the state-of-the-art in carbon dioxide conversion catalysts.

While methods and tools for the systematic and automated generation of reaction paths , such as RING (Rangarajan et al., 2012a,b, 2014) have been proposed, most of them have not been applied to carbon dioxide capture and conversion. ProCARPS (Cignitti, 2014) is a tool for a hybrid method, which uses heuristics based on knowledge of chemical interactions combined with a computational model, to generate reaction paths. This tool is implemented by the four-step method proposed

by Roh et al. (2016b). The four steps in this method are: target generation, reaction path synthesis, thermodynamic screening, and reaction network generation. By following these steps, the search space is reduced, starting from an extremely large number of reactions to the network of feasible reactions. By applying reaction path synthesis, it is possible to generate a reaction network of carbon dioxide conversion reactions; these reactions can then be investigated for implementation in processes and process networks.

2.4.4 Sustainability within CCU

The importance of sustainability analysis for carbon dioxide conversion processes has been emphasized in several review papers (Araújo et al., 2014; North and Styring, 2015; Poliakoff et al., 2015; Quadrelli et al., 2011). Generally, carbon footprint or net carbon dioxide emission of a certain conversion process is used as the most significant indicator in assessing sustainability of the process.

Various methods for sustainability analysis have been developed and applied to carbon dioxide conversion processes. As von der Assen et al. (2013, 2014) and von der Assen and Bardow (2014) point out, there are common pitfalls in performing LCA of a CCU system:

1. carbon dioxide consumed by utilization (including conversion) might be considered as negative GHG emissions

2. one should decide how to allocate overall emissions between the products in the capture (captured carbon dioxide) and in the utilization (produce chemical products) processes

3. traditional LCA is not well suited to assessing global warming impact of carbon dioxide storage duration

In the first pitfall, the upstream emissions in obtaining the carbon dioxide are not always considered; in order to avoid this, the carbon dioxide utilized can not always be directly considered as negative emissions. The second pitfall results from the problem in allocating emissions to the carbon dioxide being utilized as it is not intuitive how to allocate the emissions to different products. The third pitfall is that traditional LCA does not allow for the delayed emission that result from utilization. von der Assen et al. (2013, 2014) and von der Assen and Bardow (2014) propose the use of a systematic framework to perform LCA on carbon dioxide conversion processes to avoid such problems; CO_2-based methanol (via CO_2 hydrogenation) and polymer production are used as examples to highlight their framework. Babi

et al. (2015), Kongpanna et al. (2016), and Roh et al. (2016b) suggest a method for designing sustainable carbon dioxide conversion processes involving the three-stages of process synthesis, process design, and innovative design/implementation and providing lists of applicable tools for each stage. These three stages decompose the problem and address sustainability in each stage. In the final stage, more sustainable processes are obtained by considering innovative and intensified alternatives. All the analyses performed greatly depend on the assumptions made, especially with regard to feedstock.

Beyond sustainability analysis for a fixed design of carbon dioxide conversion processes, Taghdisian et al. (2015) performed multi-objective optimization for a bi-reforming based methanol plant. This study aimed to maximize methanol production while minimizing carbon dioxide emission simultaneously. The trade-off relation between the two objective functions was given as the Pareto frontier, which showed a typical trend found in conventional chemical processes.

2.4.5 Integration of carbon dioxide utilization with other systems

For carbon dioxide conversion processes to be sustainable, they need to be integrated with infrastructure (such as for supply of raw materials and utilities, sales of products, implementation with existing technology such as reactors, catalysts or distillation columns) and other processes (such as for energy production and carbon dioxide capture). By looking at the combined system, it is possible to consider not only the individual processes, but also the interactions between them, as illustrated in Figure 2.3. In this way, better and even optimal performance of the overall systems can be achieved.

Indala (2004) and Xu et al. (2005) propose a superstructure network that involves an integrating an existing ammonia plant with various potential conversion plants producing methanol, ethanol, dimethyl ether, syngas, and so on by using the high-purity carbon dioxide byproduct. Their optimal configuration considers the following three aspects: operating margins, environmental costs, and sustainable costs. Roh et al. (2016b) also addressed the integration issue. In their study, it is assumed that an existing methanol plant, where carbon dioxide is not utilized, is integrated with a bi-reforming based methanol plant and then the effect of changing the integration switch (IS) on carbon dioxide reduction is evaluated. It is concluded that as the IS increases, the overall carbon dioxide emission decreases. Martín and Grossmann (2016) designed a CO_2 hydrogenation-based methanol production facility integrated with switchgrass gasification units that produce the syngas for methanol production. The carbon dioxide feedstock is captured from the syngas produced from the switchgrass gasification and the hydrogen feedstock is produced

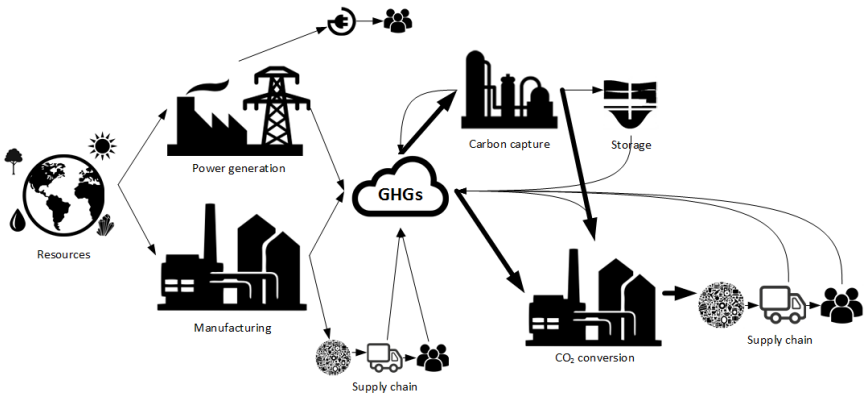

Figure 2.3. A visualization of the entire carbon capture and conversion system and the interactions. If the different processes are only considered individually, it is not possible to design around interaction. However, when the entire system is considered, it is possible to optimize while taking into account the interactions, such as those in bold considered here. (Roh et al., 2016a)

via water splitting with wind and solar power. They conclude that the designed process can only be used in regions where wind velocity and solar radiation are high enough, such as the US Midwest or the south of Europe.

Within integration of carbon dioxide utilization processes with other systems, the feedstock needs to be considered. Jones et al. (2011) designed and evaluated a sodium bicarbonate production process that utilizes flue gas directly. Minutillo and Perna (2010) as well as Nguyen (2015) design tri-reforming based methanol plants that utilize flue gas as a carbon dioxide source. Alternatively, the carbon dioxide can be captured at a reduced concentration. Frauzem (2014) considers a CO_2 hydrogenation-based methanol plant integrated with a carbon dioxide capture plant employing the monoethanolamine (MEA) solvent with a reduced purity carbon dioxide stream. Both are possible, however, the reduced purity increases the energy costs of the methanol production.

Optimization of a CCUS supply chain network is another important issue of the integration with sources of carbon dioxide. Hasan et al. (2014) developed a large-scale (nationwide, regional, and statewide) CCUS network model and determined an optimal solution that minimizes the cost to reduce stationary carbon dioxide emissions in the United States. More than 3,000 emission points and various alternatives of carbon dioxide capture technologies (absorption, adsorption, and membrane-based), utilization (enhanced oil recovery) and sequestration (in saline formations and un-mineable coal bed areas) are considered in this study. Han and Lee (2011) worked on carbon dioxide utilization and disposal infrastructure

development and its optimization in the case of South Korea. Four different carbon dioxide sources (two fired-power plants, one petroleum refinery, and one iron/ steel plant) were targeted. Manufacturing of green polymer and bio-butanol were considered as the utilization methods, while geological/ocean sequestration were considered as the disposal methods.

2.5 Ontologies

As with any problem, the sustainable design of carbon dioxide capture and utilization processes involves large amounts of information. This information needs to be organized and stored in a way that it can be used and reused. Therefore, an ontology is needed to organize the knowledge base (or database) in a way that it is systematic. An ontology is an explicit specification of a conceptualization covering a certain domain and the relations between them (Gruber, 1993). A conceptualization is a formal representation of a knowledge base, including the objects, concepts, etc. that exist within this knowledge base. In order to develop an ontology, certain terms need to be defined (Noy and McGuinness, 2001):

classes (concepts) descriptions of the concepts in the domain

slots (roles or properties) properties of the concepts to describe features and attributes

facets (role restrictions) restrictions on slots

instances individual instances of classes within an ontology form a knowledge base

In order to develop ontologies, methodologies have been developed. Noy and McGuinness (2001) propose a simple methodology for the development of an ontology. They discuss the general issues and propose an iterative approach in which the first pass is refined with more details each round. The methodology is composed of seven steps starting with defining the scope of the ontology to the instances of the classes. Gruber (1995) defines criteria for the design of ontologies:

1. Clarity: the ontology needs to be effective in the communication of the concept
2. Coherence: the ontology needs to be logically consistent
3. Extendibility: the ontology needs to be able to accommodate new information
4. Minimal encoding bias: the ontology should not depend on the notation

5. Minimal ontological commitment: the ontology should be free so that it can be specialized when needed

This method for the design of ontologies has been implemented by Singh et al. (2010), where an ontology is developed for the use in process monitoring and analysis. The result is a knowledge base containing two sections which also are linked by certain objects.

An ontology is needed to develop a structured database that facilitates the addition and extraction of information for the solution of problems. For the work of carbon dioxide capture and utilization, no ontology or knowledge base is available. However, certain information on emissions (source, quality, etc.) is available and stored; but, none of these are structured or address the design of carbon dioxide capture or utilization processes. Therefore, use of methodologies, such as that proposed by Noy and McGuinness (2001) can be implemented to develop an ontology for a knowledge base, which is structured to enable easy addition and extraction of information related to the design of sustainable carbon dioxide capture and utilization processes. This includes information on the process, materials and reactions.

2.6 Gaps and challenges

Process synthesis methods are prevalent in determining the processing route; heuristic, mathematical programming and hybrid methods have all been developed and applied to a variety of problems, including to chemical, biochemical and waste water processes. However, very few have been applied to the optimization of carbon dioxide conversion networks. This is in part due to the limited information available about such processes. Due to the novel nature of such processes and the immaturity of the information, the accurate description of the conversion alternatives is a challenge. Recently, superstructure optimization methods have been applied to determine the optimal processing route to produce a specific product or a selection of products. The application of these methods is, however, limited to considering only a small number of products or to the synthesis of capture processes; the application to multiple conversion products and the link of capture and conversion processes is missing. A wider application of these methods would enable to selection of the optimal carbon dioxide capture and conversion products and processes.

Rigorous design methods, such as those in Seider et al. (2008), and tools, such as AspenPlus (AspenPlus, 2016) and ProII (SimSci, 2016) are well developed for application in the design of chemical and biochemical processes. For carbon dioxide capture and utilization processes (specifically conversion processes), detailed

information about the reaction and catalyst, including the reaction kinetics, are needed. Without such information, the models are inaccurate, which will affect the equipment and the downstream processing. In addition, basic knowledge for process design like thermodynamics, heat and mass transfer phenomena, reaction and separation engineering is also available. Thermochemical reaction information, along with basic knowledge and experience is available for carbon dioxide conversion processes; rigorous design methods have been applied using this information to the production of methanol and other chemicals from carbon dioxide. However, most carbon dioxide conversion technologies are currently in their early stages of development, which limits the studies on carbon dioxide conversion process design.

Process intensification and integration methods have been applied to carbon dioxide capture and utilization processes. However, these cases are limited, especially in terms of the process integration and the influence that the supply chain and other processes have on the design of carbon dioxide capture and conversion processes. While the systematic methods, for example phenomena-based methods, for process intensification have been developed, they have only been applied to carbon dioxide capture and conversion processes to specific products (Kongpanna et al., 2016). Carbon dioxide capture and conversion processes have been designed, but they could benefit from process intensification as this would reduce the amount of equipment and energy required in some of the processes.

While reaction path synthesis methods and tools have been developed, carbon dioxide conversion reaction networks are dominated by heuristics and knowledge bases. Computer-aided methods and tools have been developed for use in reaction path synthesis, to facilitate the generation of reaction paths and generate more exhaustive lists of reaction. Currently, only the known reactions are investigated further. This limits the ability to find new and innovative reaction paths and networks that are not discovered previously. Especially dominant in these compilations are the reactions producing bulk chemicals (such as methanol and urea) and fuels (such as gasoline and diesel). However, with the help of tools from reaction path synthesis, the large number of additional reactions can be determined and compared. In addition, this extensive list of reactions can be screened for thermodynamic properties, ranked, or products can be selected according to their need.

Sustainability is one of the most important issues for carbon dioxide capture and utilization processes, as the motivation for developing them is to address environmental concerns. However, in carbon dioxide capture and utilization processes, there are certain pitfalls that need to be avoided in the sustainability and life cycle analyses. For carbon dioxide capture and utilization, the goal is to identify those

processes with very low carbon footprints or negative net carbon dioxide emissions. However, one should be careful in the analysis as the results depend strongly on how wide their system boundaries are chosen to be, how the feedstock and utility are assumed to be prepared, and what conventional (or reference) cases they are compared against.

Despite the application of process synthesis-design, integration, intensification, reaction path synthesis and sustainability analysis to carbon dioxide capture and utilization processes, there are areas that have not been explored or need to be further explored for these processes. The synthesis methods need to be applied to a wider range of processes and products to optimize the processes. Then, intensification and integration should be applied to more cases to overcome bottlenecks in the processes as well as ensure the optimal capture and conversion process. Reaction path synthesis methods should be applied more extensively to ensure that all promising reactions using carbon dioxide are considered. Finally, the sustainability analysis needs to be consistent and applied to all processes as this is a requirement in the design of carbon dioxide capture and conversion processes.

In the area of carbon dioxide capture and utilization, there are large amounts information, from materials (carbon dioxide emission sources to products) to technologies for the capture and utilization of the carbon dioxide, that needs to be appropriately organized and stored. Currently, this collection of technologies is lacking. A structured database is necessary for design of a database which enables the systematic storage and retrieval of the information.

As interest in carbon dioxide capture and utilization, especially conversion, grows, there is a need to sustainably design such processes. Through the development and implementation of a systematic and computer-aided framework, this can be ensured. This framework should incorporate the existing methods and tools (especially for process synthesis, design, intensification and sustainability) and adapt/develop methods and tools where needed (especially for reaction path synthesis and databases). In addition, it should be flexible enough to be applied to various carbon dioxide capture and utilization problems. Through the use of this framework, more products and feedstocks, and novel routes can be considered. Additionally, integrated and intensified solutions can be presented. The objective of this work is to design sustainable carbon dioxide capture and utilization processes using a framework that addresses the aforementioned gaps.

Chapter 3

Framework

Summary and significance:

In this chapter, the developed framework for the sustainable design of carbon dioxide capture and conversion processes along with the necessary computer-aided methods and tools is presented. The developed computer-aided framework adapts a 3-stage approach for sustainable design (Babi et al., 2015), comprising of synthesis, design and innovation. Each stage has its own workflow and data flow, where the outputs of one stage serve as the inputs to another; these are described in detail in this chapter. There are various methods and tools, which are included in the framework. In Stage 1, which uses a superstructure-based method to find the optimal route(s), the framework incorporates reaction path synthesis, an especially structured database for the storage of information, and the software interface, Super-O. Stage 3 makes use of process integration methods, phenomena-based process intensification and a method for hybrid distillation-membrane process design. Finally, the framework includes simulation software, analysis tools and evaluation criteria, which are also presented.

Outline:

Carbon dioxide capture and utilization processes are one method to address the environmental concerns associated with carbon dioxide emissions. However, the processes need to be sustainable; a systematic, computer-aided framework has been developed to facilitate the design and ensure their sustainability. Through the implementation of the framework, the overall design problem, given a feedstock, or set of feedstocks, determine the optimal route and configuration to a product or set of products, which is mathematically formulated according to Equation 3.1, is addressed (Duran and Grossmann, 1986).

$$\begin{aligned} &\min / \max_{x,y} F_{obj} = C^T y + f(x) \\ s.t. \quad &r(x) = 0 \\ &s(x) + B(y) \leq 0 \\ &x \in R^n, \quad y(0,1)^l \end{aligned} \tag{3.1}$$

F_{obj} is the objective function, which is a function of the continuous variables, x, and discrete variables, y. The continuous variables are related to processing information, including flow rates, design parameters and so on, while the discrete variables are related to decisions, including those related to topology. C^T is a matrix of cost coefficients related to the discrete variables, such as capital costs. $f(x)$ is the cost related to the continuous variables, such as material prices. The objective function is subject to linear, $r(x) = 0$, and non-linear, $s(x) + B(y) \leq 0$, constraints. These equations yield a mixed-integer (non)-linear programming problem (MI(N)LP).

The developed framework is based on the 3-stage approach to sustainable design introduced by Babi et al. (2015). By decomposing the problem into three stages, the complexity of the problem can be managed, as otherwise it can be computationally infeasible to solve the entire problem in one stage. The overall 3-stage framework is shown in Figure 3.1. The detailed workflow and data flow is presented in Sections 3.2 - 3.4 and the methods and tools spanning across the stages are presented in Section 3.5.

3.1 3-stage approach

In the 3-stage approach, the problem is decomposed into three sub-problems: (1) synthesis, (2) design and (3) innovation. Each of these stages has an output that serves as the input for the subsequent stages. The stages enable the solution of the problem, which might not be computationally possible in a single stage. In each stage, the search space is reduced and more details are considered. Qualitatively correct but simpler models are used to select from the large number of alternatives

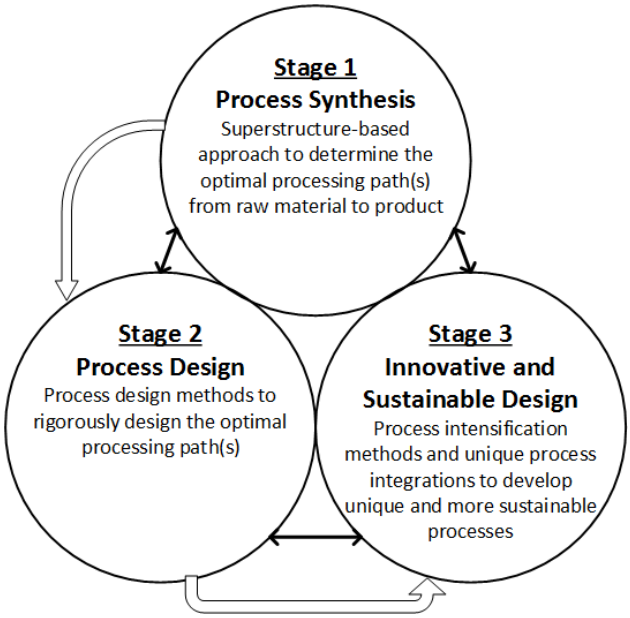

Figure 3.1. An overview of the adapted 3-stage approach.

in Stage 1. In this way, infeasible alternatives are discarded after Stage 1 to avoid the time spent in design and modeling of these alternatives. The remaining alternatives are then designed and analyzed in Stage 2. Finally, in the third stage, more sustainable alternatives are found for designs from the second stage. The stages function independently, so long as the necessary input information is provided.

Across the three stages, the overall formulation remains the same. However, the scale considered, complexity of the models and the number of alternatives vary between stages. In the first stage, the models are simple so that a large number of alternatives can be considered. The inputs of this stage are the process parameters needed for the simple models and the output is the optimal topology along with mass and energy flows. This ouput is then used as the input in the second stage. For the second stage, rigorous process models are considered for the small number of alternatives. The result of detailed design includes the stream and equipment information and the analysis results provide the targets for improvement. These targets are then used as the input for the final stage. Here, the selected process is described by phenomena-based models. These are then used to obtain improved design alternatives that address the targets; these alternatives are then designed rigorously and analyzed to ensure the specifications are met. The characteristics of the models and data of the different stages are listed in Table 3.1 (adapted from Bertran et al. (2017)).

Table 3.1. The problem characteristics, data flow, optimization problem form and problem variables across the three stages (adapted from Bertran et al. (2017).)

	Stage 1	**Stage 2**	**Stage 3**
No. of alternatives	large	medium	small
Complexity	low	high	high
Scale	interval	unit operation	phenomena
Inputs	process parameters	topology, mass flows, energy flows	base case design (equipment design, stream tables, economic parameters, sustainability indicators), targets for improvement
Outputs	topology, mass flows, energy flows	base case design (equipment design, stream tables, economic parameters, sustainability indicators), targets for improvement	improved design (equipment design, stream tables, economic parameters, sustainability indicators)
Model	shortcut models	rigorous process models	phenomena-based process models

3.2 Stage 1: Synthesis

Stage 1, the synthesis stage, is a decision-making problem; it involves the determination of the optimal processing route(s) converting raw material to product. This can be more specifically defined as, given a carbon dioxide containing feedstock or set of carbon dioxide containing feedstocks, determine the optimal sequence, including selection of optimal equipment, to produce a product or set of products. A superstructure-based method developed by Quaglia et al. (2012, 2015) and extended by Bertran et al. (2017) is used to address this problem. A superstructure is a representation of the alternatives where boxes represent process alternatives and arrows are feasible connections between alternatives (Bertran et al., 2017). Elements in the superstructure are organized in terms of processing steps and processing intervals, where each column in the superstructure represents a processing step and the alternatives within them are represented by processing intervals (Bertran et al., 2017). This is called a Processing Step-Interval Network (PSIN) and organizes the network according to the representation in Figure 3.2.

The PSIN representation provides an organized superstructure that can represent processing networks of varying scales: from a part of a process to a network of processes (Bertran et al., 2017). Depending on the scale and level of detail, a processing interval is used to represent a task, a unit operation, multiple units, or a complete process.

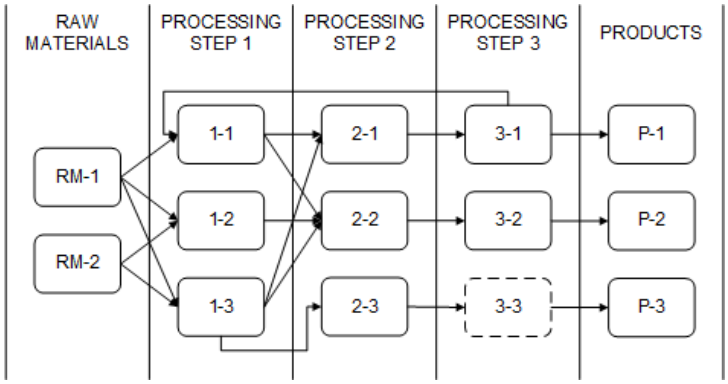

Figure 3.2. Visual representation of the Processing Step-Interval Network representation used in Stage 1 of the framework (Bertran et al., 2017).

A generic optimization model for the synthesis of these processing networks problems using the PSIN representation was proposed by Quaglia et al. (2012) and extended by Bertran et al. (2017). The extension added the following features: location dependency, multiple utility locations, material assignments modified for capacity optimization, and capital cost linearization (Bertran et al., 2017). All intervals in the superstructure are modeled with the same set of equations representing a sequence of tasks: mixing, reaction, waste removal, product separation, and utility consumption. A schematic diagram of the generic interval is shown in Figure 3.3.

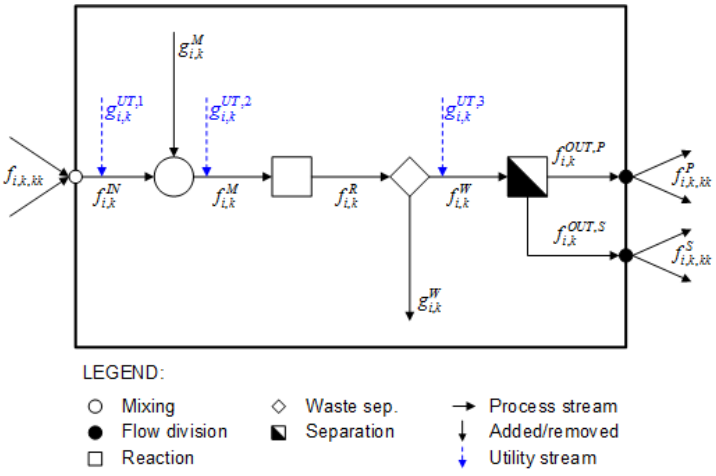

Figure 3.3. The generic interval used to represent the superstructure alternatives (Bertran et al., 2017).

The superstructure is modeled by a series of equations within the overall formulation in Equation 3.1 (Bertran et al., 2017). These equations are broken down into

the objective function, linear constraints and non-linear constraints. The linear constraints are comprised of mass balances, capital costs and composition constraints (Bertran et al., 2017) and the non-linear constraints contain connection equations and logic constraints (Bertran et al., 2017).

Objective function

$$\max Z = S^{PROD} - C^{RAW} - C^{CHEM} - C^{UT} - C^{TR} - C^{WASTE} - \frac{C^{CAP}}{\tau} \tag{3.2}$$

where

$$S^{PROD} = \sum_k \sum_i P_k^{PROD} f_{i,k}^W \tag{3.3}$$

$$C^{RAW} = \sum_k \sum_i P_k^{RAW} f_{i,k}^W \tag{3.4}$$

$$C^{CHEM} = \sum_k \sum_i P_i^{CHEM} g_{i,k}^M \tag{3.5}$$

$$C^{UT} = \sum_k \sum_{ut} P_{ut}^{UT} f_{ut,k}^{UT} \tag{3.6}$$

$$C^{TR} = \sum_{k,kk} P_{k,kk}^{TR} \eta_{k,kk} \sum_i f_{i,k,kk} \tag{3.7}$$

$$C^{WASTE} = \sum_k \sum_i P_i^{WASTE} (g_{i,k}^W) \tag{3.8}$$

$$C^{CAP} = \sum_k inv_k \tag{3.9}$$

The objective is to maximize EBIT (earnings before interest and tax), where Z is the objective function, S^{PROD} is the sales, C^{RAW} is the cost of raw material(s), C^{CHEM} is the cost of chemicals, C^{UT} is the cost of utilities, C^{TR} is the cost of transportation, C^{WASTE} is the cost of waste, C^{CAP} is the capital cost and τ is the project lifetime. The parameter P is the price, the variable f is the component flow rate, the variable g is the added or removed component flow rate, and η is the transportation distance. The subscripts i, k, kk, and ut are for component, starting interval, ending interval, and utilities, respectively. The superscripts $PROD$, RAW, $CHEM$, UT, TR, $WASTE$, CAP indicate the product, raw material, chemicals, utilities, transportation, waste and capital cost elements. The superscripts W and M are for the points after the waste separation and after the mixing for the flow in the intervals. inv is the investment cost. While the objective function in this case is only economic, all the alternatives will additionally be ranked by $NetCO_2$ so as to ensure the sustainability of the alternatives.

Equality constraints

Mass balance The mass balances are constraints to ensure that the mass balance closes.

$$f_{i,k,kk} = f^{P}_{i,k,kk} + f^{S}_{i,k,kk} \tag{3.10}$$

$$f^{IN}_{i,k} = \sum_{kk} f_{i,k,kk} \tag{3.11}$$

$$g^{M}_{i,k} = \sum_{ii} f^{IN}_{ii,k} \mu_{i,ii,k} \tag{3.12}$$

$$f^{M}_{i,k} = f^{IN}_{i,k} + g^{M}_{i,k} \tag{3.13}$$

$$f^{R}_{i,k} = f^{M}_{i,k} + \sum_{r} f^{M}_{react,k} \theta_{react,r,k} \gamma_{i,r,k} \frac{MW_i}{MW_{react}} \tag{3.14}$$

$$f^{W}_{i,k} = f^{R}_{i,k}(1-\delta_{i,k}) \qquad \forall k > N^{RAW} \tag{3.15}$$

$$g^{W}_{i,k} = f^{R}_{i,k} - f^{W}_{i,k} \qquad \forall k > N^{RAW} \tag{3.16}$$

$$f^{OUT,P}_{i,k} = f^{W}_{i,k} \sigma_{i,k} \tag{3.17}$$

$$f^{OUT,S}_{i,k} = f^{W}_{i,k} - f^{OUT,P}_{i,k} \tag{3.18}$$

$$g^{UT,1}_{ut,k} = \sum_{i} \beta^{1}_{ut,k} f^{IN}_{i,k} \tag{3.19}$$

$$g^{UT,2}_{ut,k} = \sum_{i} \beta^{2}_{ut,k} f^{M}_{i,k} \tag{3.20}$$

$$g^{UT,3}_{ut,k} = \sum_{i} \beta^{3}_{ut,k} f^{W}_{i,k} \tag{3.21}$$

$$g^{UT}_{ut,k} = g^{UT,1}_{ut,k} + g^{UT,2}_{ut,k} + g^{UT,3}_{ut,k} \tag{3.22}$$

$$f^{OUT,1}_{i,k} = \sum_{k} f^{1}_{i,k,kk} \qquad \forall k < (N^{RAW} + N^{INT} + 1) \tag{3.23}$$

$$f^{OUT,2}_{i,k} = \sum_{k} f^{2}_{i,k,kk} \qquad \forall k < (N^{RAW} + N^{INT} + 1) \tag{3.24}$$

$$f^{W}_{i,k} = \sum_{l} f^{source}_{i,k,l} \qquad \forall k < (N^{RAW} + 1) \tag{3.25}$$

The parameters represent different parameters in the tasks; μ is the mass mixing fraction, θ is the conversion, γ is the stoichiometric coefficient, MW is the molecular weight, δ is the waste separation factor, σ is the product separation factor, and β is the utility addition factor. Additionally, N is the interval number. The superscripts define different points in the interval; P is the primary outlet stream from an interval, S is the secondary outlet stream from an interval, IN is the inlet, R is the point after the reaction task, OUT is the outlet from product separation, $UT,1$, $UT,2$

and $UT,3$ are the first, second and third utility addition points, 1 is the first utility point, 2 is the second utility point, 3 is the third utility point, INT is the number of intervals and *source* is the source. The subscripts *react* and r are the reactant and reaction, respectively, and the subscript ii represents the mixing component.

Capital costs The capital cost constraints describe the flow-rate based cost model and the linearization.

$$F_k^{CAP} = \sum_i f_{i,k}^M \tag{3.26}$$

$$F_k^{CAP} = \sum_j F_{k,j}^D \tag{3.27}$$

$$F_{k,j}^D = FPOINT_{j+1} piece_{k,j} \tag{3.28}$$

$$inv_k = \sum_j A_{j,k} F_{k,j}^D + B_{j,k} piece_{k,j} \tag{3.29}$$

Here, the F are the total flow rates, the superscript D signifies disaggregated, $FPOINT$ is the point flow in the linearization, *piece* is the binary variable for the interval considered in the piecewise linearization, and A and B are the coefficients for the linearization.

Raw material composition These constraints define the mass balance based on the composition of the streams.

$$f_{i,k}^W = \phi_{i,k} F_k^{RAW} \tag{3.30}$$

$$F_k^{RAW} = \sum_i f_{i,k}^W \tag{3.31}$$

The parameter ϕ is for the mass fraction.

Inequality constraints

Connection equations The connections equations describe the connection of intervals in the superstructure.

$$f_{i,k,kk}^1 \leq f_{i,k}^{OUT,P} S_{k,kk}^P \tag{3.32}$$

$$f_{i,k,kk}^2 \leq f_{i,k}^{OUT,S} (SS_{k,kk} - SS_{k,kk}^P) \tag{3.33}$$

$$y_{kk} \omega_{kk} \leq y_k \tag{3.34}$$

ω is the binary variable indicating whether the interval is a mixer (two streams enter the interval), SS is the binary variable for the superstructure connection, and y is the binary variable for the selection of intervals.

Logic constraints The logic constraints are used to limit the solutions to feasible and desirable alternatives by using the binary variables for the selection of the intervals.

$$f_{i,k}^{W} \leq y_k M \tag{3.35}$$

$$g_{i,k}^{W} \leq y_k M \tag{3.36}$$

$$y_k \leq \sum_i f_{i,k}^{W} \frac{M}{1000} \tag{3.37}$$

$$\sum_i f_{i,k}^{IN} \leq y_k M \tag{3.38}$$

$$\sum_{kk} y_{kk} \upsilon_{kk,step} \leq 1 + \sum_k \sum_{kk} (\upsilon_{k,step} S_{k,kk} \omega_{kk}) \tag{3.39}$$

$$FPOINT_j piece_{k,j} \leq F_{k,j}^{D} \tag{3.40}$$

M is the "big M" variable, which is an artificial variable that is significantly big, which is needed for the solution of the problem containing "greater-than" constraints. υ is the allocation of the interval to a step. The "big M" variable is an artificial variable that is needed to

The resulting optimization problem is solved by solving all equations (Bertran et al., 2017). This problem takes the form of a Mixed-Integer Nonlinear Program (MINLP) or a Mixed-Integer Linear Program (MILP) depending on the form of the models. If all the models for technologies are linear or any non-linear models are approximated via linear models, the problem is an MILP (Bertran et al., 2017). The mathematical solution approach for the optimization problem depends on the type of problem. The steps used to solve this synthesis problem are described in Section 3.2.1.

3.2.1 Workflow and data flow

This stage is broken into three steps: (1) problem definition, (2) superstructure generation and data collection, and (3) solution of the optimization problem. The workflow and data flow are shown in Figure 3.4.

Step 1.1 is the problem definition. The objective is to define the synthesis problem that needs to be solved by specifying the available raw materials, the desired products, the location(s), the number of processing steps, and the available technologies able to perform the tasks involved in each of the considered steps (Bertran et al., 2017). During this step, not all the mentioned characteristics need to be specified. For example, a single raw material can be selected, such as flue gas

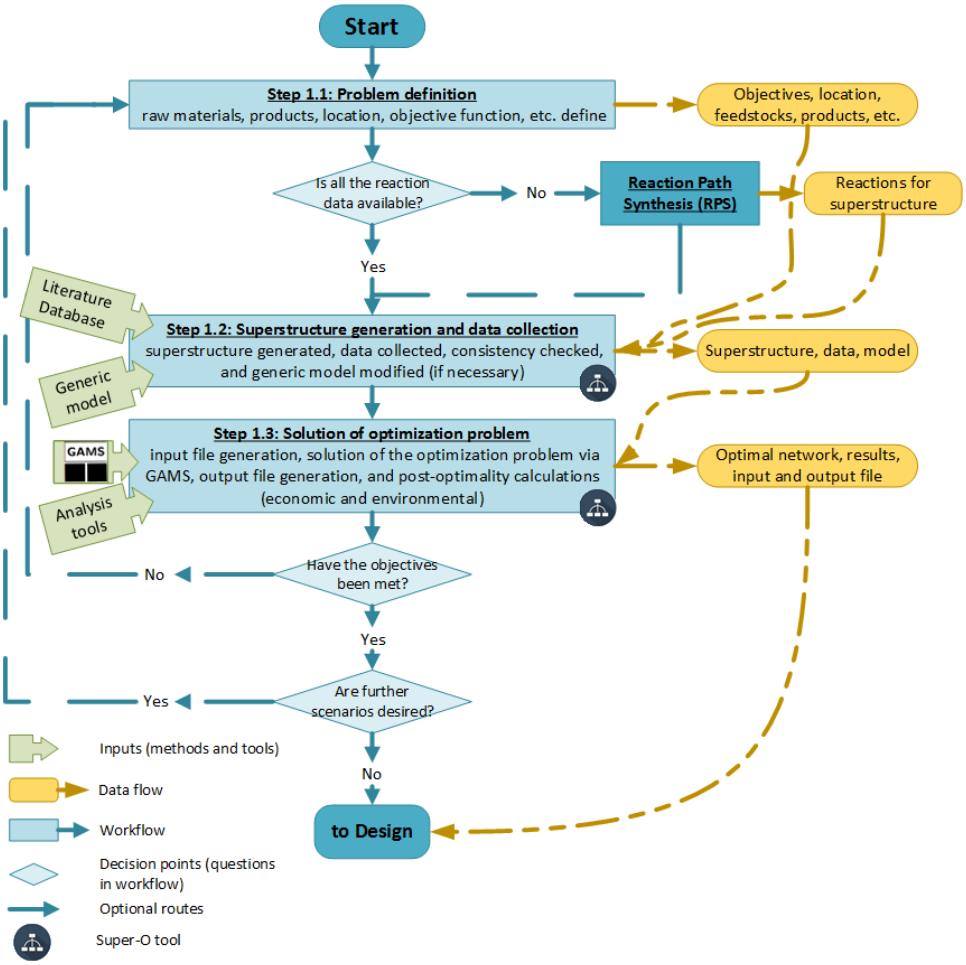

Figure 3.4. The workflow and data flow for Stage 1 of the developed framework along with the input methods and tools (adapted from Bertran et al. (2017)).

from a coal-fired power plant, or a group of raw materials can be chosen, such as power plant flue gases.

After the first step, there is a decision of whether the reaction data is available or not. If the reaction information is complete, the user can proceed to Step 1.2. Otherwise, the user first proceeds to Reaction Path Synthesis (RPS), which is described in Section 3.2.3, to generate all thermodynamically feasible reactions satisfying the objectives.

Step 1.2 is superstructure generation and data collection. The objective of Step 1.2 is to collect all the necessary data for the problem that has been defined and to generate a superstructure of alternatives (Bertran et al., 2017). To achieve this,

the complete problem formulation from Step 1.1 is needed. Step 1.2 is further decomposed into the following: data collection, superstructure generation, selection of the generic mathematical model from a library and modifications to it in order to suit the specific problem being considered. In data collection, the data is collected from various literature sources, online databases or estimated via thermodynamic models. This data can also be stored and retrieved from an especially structured database (see Section 3.2.2). Then, the superstructure, in the form of a PSIN, is generated through data on connections, technolgies and materials. Finally, if changes to the model are necessary (modification of the objective function, etc.), this is performed. Parts of this step are made easier by the use of the interface, Super-O (see Section 3.2.4). The superstructure with the data is then transfered to the next step.

Step 1.3 is the solution of the optimization problem. This is achieved by employing solvers from an external software tool (GAMS) through the user interface Super-O (see also Section 3.2.4). The inputs to the solver are the generic model and an input file with all the necessary problem data (model parameters, material data, cost data, etc.). The outputs from the solver is given in an output file containing the optimal values of the objective function, the corresponding optimization variables, and all other process variables.

Once these three steps have been followed, the user needs to determine if the objectives have been met and if further scenarios, variations in the problem definition (objective of the synthesis problem) are desired. If the objectives have not been met or if other scenarios are desired, the user returns to Step 1.1 and repeats the steps until the objectives have been met and no other scenarios are desired. The resulting optimal processing route(s) and the corresponding information is taken to Stage 2.

3.2.2 Superstructure database

All the information involved in the superstructure generation needs to be stored; this includes the connections, materials, technologies, parameters and reactions. In order to ensure that this information can be retrieved and added upon for different situations and problems that are solved, a database has been developed. This database is organized according to an ontology, which facilitates the easy addition and extraction of data (Bertran et al., 2017). In total there are three sections of data, where the first two are divided into materials and intervals, which are united by basic data, the third section. Materials represent the arrows in the superstructure; these materials need data about composition and prices. The intervals are split into tasks: mixing, reaction, waste separation and product separation; additionally,

there is the addition of chemicals and utilities. All these tasks have data on the parameters, mixing ratio, reaction conversion, and waste and product separation factors. Furthermore, the intervals need the data describing the location in the superstructure in terms of steps. The basic data is either shared by both material and technology sections or multiple elements of the sections. The component information, including properties, reactions, with the stoichiometry, and locations are basic data. In order to store all this data in a way that makes it systematic and easy to use, the ontology depicted in Figure 3.5 is used.

Basic Data Information that is shared across the other sections or needed by multiple items in a section is stored here. There are three elements of this section: components, reactions and locations. Components represent the chemical compounds that comprise the materials and are needed to define reactions, mixing, separation and other tasks. Compounds are stored according to component ID. The data that needs to be provided for these includes molecular weight and pure component properties. The reactions that are present in the intervals are stored first according to reaction sets and subsequently reaction ID. In this section, the stoichiometry of the reactions and their sets is stored. Finally, the locations which are used to define the materials and the technologies are stored.

Materials Information about the materials, which are the arrows in the superstructure, is stored in this section. The section is split into: feedstocks, materials, products and utilities. The feedstock and product have data on the location, composition, demand or availability, and price, where the composition is described by the components from the basic information. The utilities contain information on the heating values and the prices. The materials are all connections in the superstructure and are only stored by name.

Technologies The data for the intervals is stored in this section. First, the parameter data for the different tasks is stored: mixing task, reaction task, waste separation task and product separation task. For the mixing task, the chemical compound being mixed, the base compound for the mixing, and the ratio of mixing are the data that are needed. The reaction task stores the conversion and the key reactant of the reaction in the intervals. This makes use of the reaction list from the basic data section with the addition of the data relevant to the specific interval. In the waste and product separation task, the separation factors of the various compounds present in the interval are stored using the components from the basic data section. In utility mixing, the mixing parameters of the utilities, from

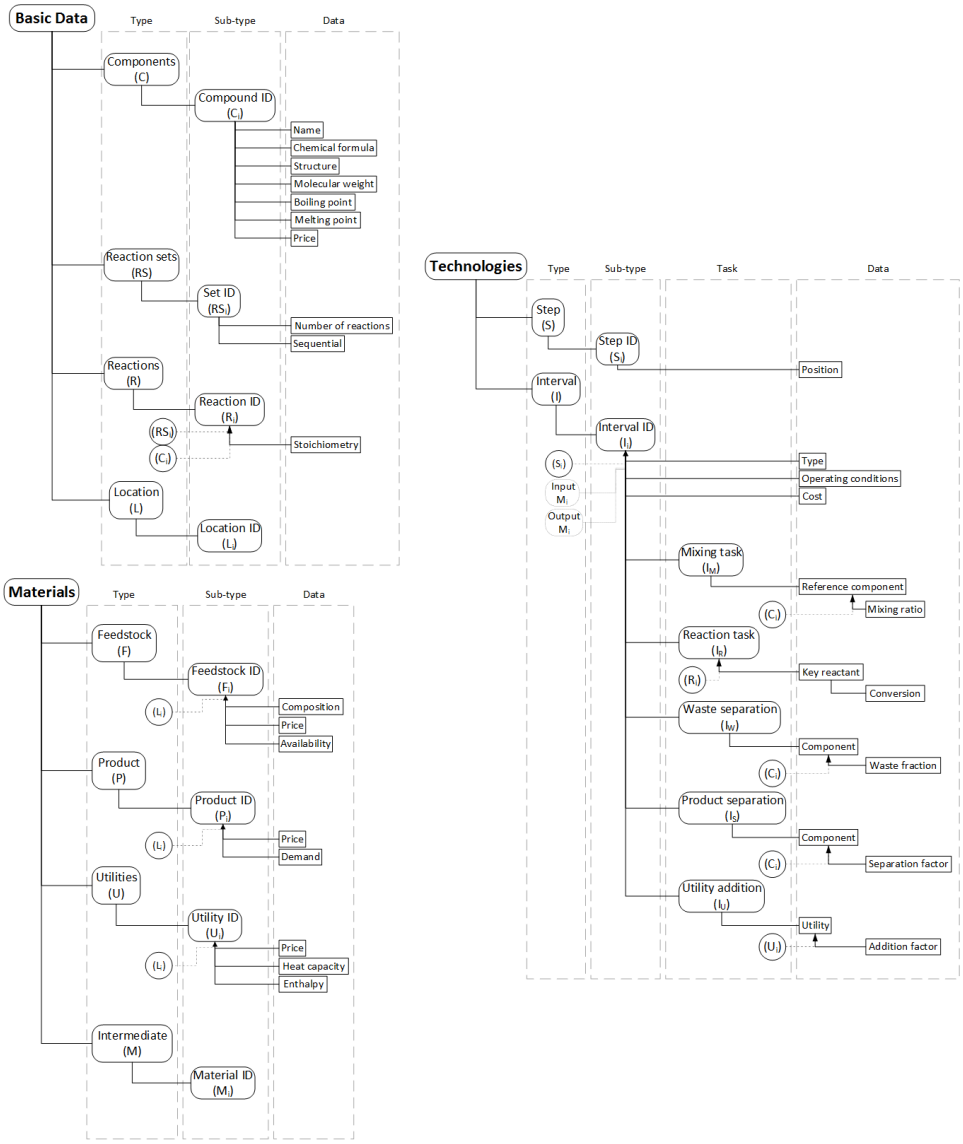

Figure 3.5. The structure of the database used to store the data for Stage 1 (adapted from Bertran et al. (2017)).

the materials section, at the different mixing points is specified. Finally, the position in the superstructure is stored; this is achieved by storing the processing step and connections. A material, from the materials section, is defined at every inlet and outlet; when the inlet of one interval matches the outlet of another, a connection is formed. In this way, the connections are easily stored and new connections for new intervals can be easily added.

The statistics of the developed database for carbon dioxide capture and utilization are listed in Table 3.2. Further details on the database can be found in Appendix B.1.

Table 3.2. The statistics of the superstructure database for carbon dioxide capture and utilization processes.

Number of feedstocks	4
Number of technologies	91
Number of utilities	3
Number of products	13
Number of components	36
Number of reactions	37
Number of steps	24

3.2.3 Reaction path synthesis (RPS)

After the first step in the first stage, the user can decide if there is sufficient reaction information to satisfy the objectives of the synthesis stage. If this is not the case, reaction path synthesis is performed to generate all feasible reactions. Reaction path synthesis involves seven steps, as shown in Figure 3.6.

In Step a, the objectives are defined. Based on the objectives of the synthesis stage, objectives for the types of reactions and products of the reactions are defined. This includes the number of stages in the reactions and the components that are considered as products. Once the objectives are defined, Step b is the generation of all the products. The products are generated using computer-aided molecular design (CAMD) methods and tools. The constraints for these products, such as number and type of functional groups and chain length, have been defined by the objectives in the previous steps. CAMD generates the molecules fulfilling the objectives and satisfying the constraints by combining groups according to combinatorial rules. The list of possible products for the reactions is thereby generated in this step. Step c is then the generation of all the reactions from carbon dioxide as a reactant to the products generated in the previous step. This step makes use of a reaction path synthesis (RPS) tool, ProCARPS (Cignitti, 2014). This tool makes use of stoichiometric balances and rules about the connection of certain groups (valence electrons available for bonding). As the primary reactant, carbon dioxide, and product, determined in the previous step, are set, any co-reactants and byproducts need to be determined using the tool. One stage ($A+B \leftrightarrow C(+D)$), two stage ($A+B \leftrightarrow E(+F)$; $E+G \leftrightarrow C(+D)$) or more stage reactions can be generated via this tool. In these reactions, A is CO_2, C represents a product determined in the second step, B and G are co-reactants which are calculated using the tool, E

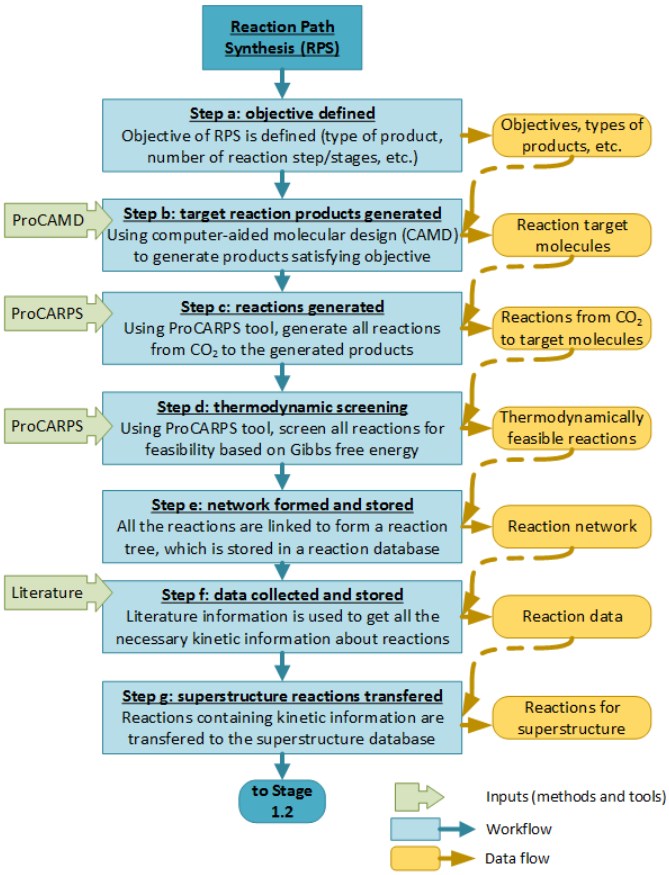

Figure 3.6. Detailed Reaction Path Synthesis framework with the corresponding workflow and data flow and the necessary methods and tools.

are intermediates also from the list of products determined in the second step, and D and F are byproducts which are cycled through. As a result of this step, all the reactions are generated linking carbon dioxide with the generated products in various ways. Then, Step d screens all these reactions for thermodynamic feasibility. To achieve this, the Gibb's free energy ΔG is calculated and used to eliminate thermodynamically infeasible reactions. In Step e, the remaining feasible reactions are connected to form a reaction tree. When the product matches a reactant of another reaction, these are linked. This reaction tree and the reactions in it are stored in a database. In Step f, literature is scoured for data on the reactions to verify reactio kinetics. Therefore, using literature, the kinetics of the reactions in the network are verified and stored. Then, those reaction with kinetic and thermodynamic data are transferred to the superstructure database in Step g.

3.2.3.1 Reactions database

For the ease of use and the storage of the reactions for future investigation and use in additional case studies, the results of the different stages of reaction path synthesis need to be stored along with the reaction information obtained from literature. Therefore, a reactions database is developed. This database is structured to organize the information according to the steps of reaction path synthesis and the information obtained in them. The results of each step are stored in separate sections with the necessary information as illustrated in Figure 3.7.

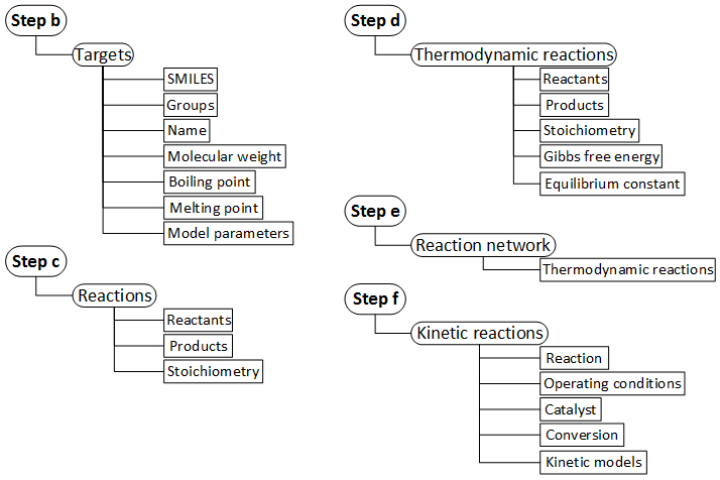

Figure 3.7. The different sections of the RPS database and the data that it contains.

The reaction path database currently contains the information as listed in Table 3.3. More details on the types of products and the reactions generated are described in Appendix B.2.

Table 3.3. The statistics of the reaction path synthesis database for carbon dioxide capture and utilization processes.

Product targets	Step b	approximately 100
Single and multi-step reactions	Step c	over 2000
Thermodynamically feasible reactions	Step d	over 100
Reaction tree	Step e	1
Reactions with published kinetic data	Step f	37

3.2.4 Super-O

Parts of the Stage 1 workflow, indicated by the “Super-O logo” in Figure 3.4, are implemented in a software interface named Super-O (Bertran et al., 2016). It has

been developed in the C# platform and it automates most of the tasks in Steps 1.2 and 1.3. For given data on a problem superstructure, the Super-O interface is able to organize the data (for the input file), do consistency checks, give a visual representation of the superstructure, linearize any nonlinear functions, allow access to the model for modifications if necessary, solve the optimization problem, and open an output file of the results (Bertran et al., 2017). Further details about the structure of Super-O and its connection to the other tools can be found in the Appendix C.

3.3 Stage 2: Design

In Stage 2, the detailed design, simulation and analysis of the optimal processing route(s) is performed. This problem can be more specifically defined as: given the flowsheet topology, mass balances and energy balances, determine the detailed equipment configuration, operation and performance specifications. The inputs are: the processing route and the associated parameters provided from the previous stage or independently. The outputs are: the detailed process information (including flow rates, utilities, and equipment sizing), the analyses (providing the economic indicators, sustainability metrics and environmental impacts), and the targets for improvement.

This stage is mathematically defined by the general design formulation (Equation 3.1). As given in Table 3.1, this stage involves the use of detailed process models for the equality constraints and design specification and constraints for the inequality constraints, with more complex models (in the unit operation scale) compared with those used in Stage 1. There are fewer alternatives because the flowsheet (processing route) is fixed and the complexity of the process models is increased, as more details are required to accurately describe the process.

3.3.1 Workflow and data flow

Stage 2 implements traditional process design methods, which are highlighted by the three-step procedure in Figure 3.8, showing the workflow, data flow and then incorporated methods and tools. This stage involves three steps: (2.1) detailed design and simulation, (2.2) process optimization, and (2.3) analysis. Note that steps 2.1 and 2.2 of this stage may be bypassed when the processing route together with detailed plant and/or simulation data is available, as in a retrofit problem.

In Step 2.1, the basic process flow diagram is needed to provide the topology (the unit operations and their interconnections). In addition, the basic design information is necessary for these units, including operating conditions, reaction

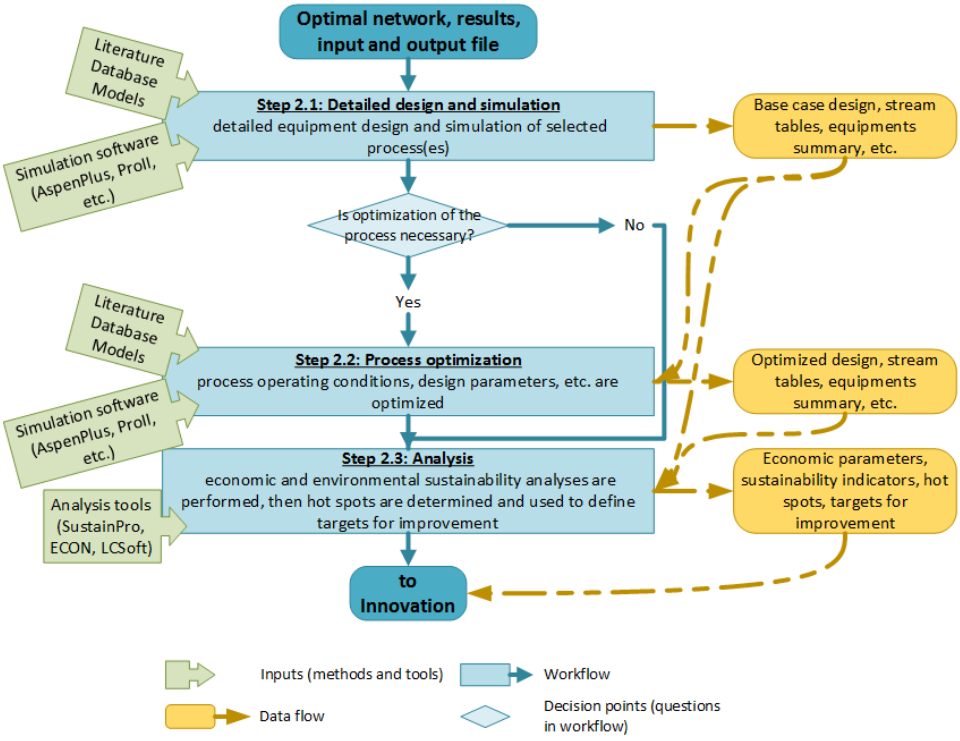

Figure 3.8. The workflow and data flow for Stage 2 of the developed framework along with the input methods and tools (adapted from Bertran et al. (2017)).

conversions, and feed and product material information and requirements. This information is obtained from literature, databases and using design calculations (as outlined in process design textbooks, including *Process and Product Design Principles* (J. D. Seader, 2010)). Using this basic information, the base case process is designed and simulated using simulation software (such as Aspen Plus (AspenPlus, 2016) or SIMSCI ProII (SimSci, 2016)). The result is a base case design with detailed information on the streams and equipment.

After Step 2.1 the user determines if the process has or has not been optimized, in terms of operating conditions. If it has, further optimization is not always necessary, and therefore the user can also proceed directly to Step 2.3. If it has not, in Step 2.2, the base-case design is optimized using standard design and simulation software to determine the optimal process, including operating conditions. The output of Step 2.2 is also the detailed information on streams and equipment for the optimal design.

Finally, in Step 2.3, the detailed stream and equipment information is used to analyze the process for sustainability (economic and environmental). The tools

that are used here include economic analysis software, such as ECON (Saengwirun, 2011), sustainability analysis software, such as SustainPro (Carvalho et al., 2013), and life cycle analysis software, such as LCSoft (Kalakul et al., 2014). The sustainability indicators and economic parameters of the process are calculated to determine the targets for further improvement of the optimized base-case. These targets are the hot spots or areas with the largest potential for improvement. For example, with the results of the sustainability analysis (via SustainPro (Carvalho et al., 2013) or another software tool), indicators of material value added or energy and waste cost can show where product or energy are being lost, so that adjustments could be made (in Stage 3) to further improve the process and make it more sustainable.

The result of this stage is a detailed process design and analysis of a process including hot spots (or targets) which can be used as inputs for Stage 3, if further improvements are necessary.

3.4 Stage 3: Innovation

In the final stage, Stage 3, the targets for improvement are addressed. This is done by applying unique process integration, process intensification and hybrid methods. The input to this stage is the output from the previous stage, the process design with the stream and equipment information, analysis results, and targets for improvement. The output of this stage is the final, more sustainable design and the corresponding equipment and stream information. Depending on the targets, either a single method or a combination of methods is used; the workflow and data flow is shown in Figure 3.9.

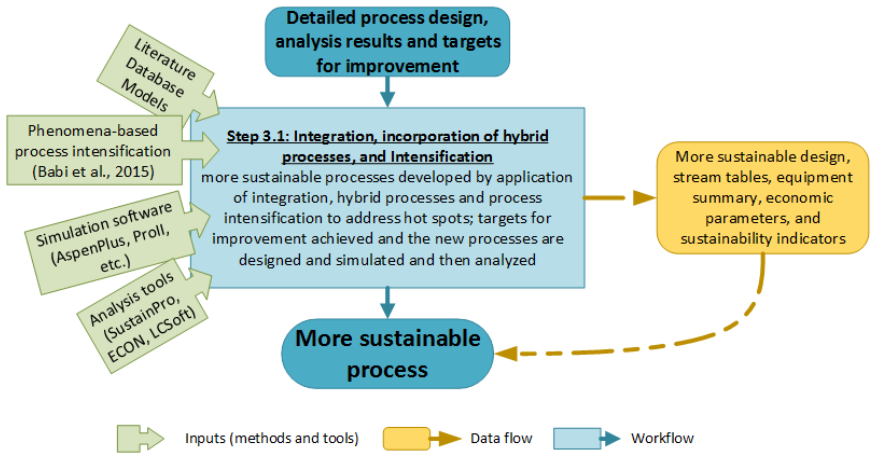

Figure 3.9. The workflow and data flow for Stage 3 of the developed framework along with the input methods and tools.

Stage 3 is especially important for existing processes where the desire is to find more sustainable process alternatives, that is, the retrofit problem.

3.4.1 Process integration

Carbon dioxide capture and utilization processes are often designed and optimized individually. However, a consideration of the interactions between processes is particularly important. Therefore, process integration can be applied; by performing heat and/or mass integration (Klemeš et al., 2013) of the integrated processes, the trade-offs can be accounted for. In carbon dioxide capture and utilization processes, the connection between the capture and utilization are important as the composition and amount of carbon dioxide from the capture process affects the conversion process. Moreover, the purity of the captured carbon dioxide, affects the energy consumption and design of the capture process. However, there is often a trade-off between these two elements. Therefore, by expanding the system boundary from the individual processes to the integrated processes, as shown in Figure 3.10, it is possible to improve the overall sustainability and optimize the energy consumption of the integrated process. Integration can already be considered in Stage 2 and should be performed in Stage 3 if it has not been already.

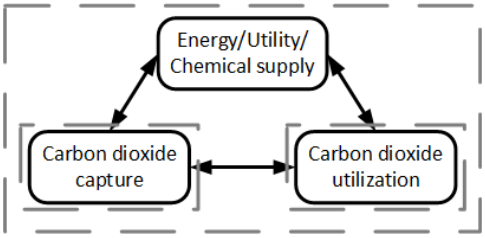

Figure 3.10. An example of extending the system boundaries from the capture process and the utilization process individually, to considering the integrated system with energy/utility supply.

3.4.2 Phenomena-based process intensification

In addition to considering the possible integration options, process intensification methods can be used to generate innovative and intensified process alternatives. Intensified equipment combines the tasks of traditional unit operations into one intensified operation, thereby, reducing size, energy and/or waste. Process intensification methods, such as the method proposed by Lutze et al. (2013) and extended by Babi et al. (2015), can be applied to obtain targeted process improvements; the

phenomena-based method reduces the scale to the phenomena-scale to enable the generation of unique equipment alternatives.

The developed method for phenomena-based synthesis and design consists of six steps: problem definition, process analysis, phenomena identification, flowsheet generation, screening, and optimization (Lutze et al., 2013; Babi et al., 2015). The targets for improvement that have been identified are translated into the objective in the first step of this method. Then, the base-case design from Stage 2 is analyzed for mass and energy balances in the second step. Additionally, in this step, the flowsheet is transformed into a task-based and then phenomena-based flowsheet; the hot-spots and the targets for improvement are also linked to specific phenomena. In the third step, desirable phenomena, which address the targets, are identified using different algorithms for component properties and mixing properties; additionally, information on the phenomena is retrieved from a database. In the fourth step, the phenomena are connected to form simultaneous phenomena building blocks (SPBs) (Lutze et al., 2013; Babi et al., 2015), which are linked to form entire processes. These connections are formed with the help of connectivity rules and with logical and structural constraints. The alternatives may or may not include intensified equipment. Subsequently, in the fifth step, the economic, environmental and LCA analyses of the alternatives are performed. Finally, the objective function is calculated and the processes are ranked. These processes are more sustainable as they satisfy the objective function and the performance criteria. However, by generating the alternatives at the phenomena level, the more sustainable alternatives can consider new equipment and by addressing the targets, more sustainable alternatives are ensured.

3.4.3 Hybrid processes

In the cases where distillation is a hot spot with high utility consumption, hybrid processes can be considered according to the method proposed by Tula et al. (2017). Hybrid distillation-membrane separation schemes can be synthesized and designed via this method. It takes into account the mixture and its properties and the challenges of the individual unit operations. The developed method consists of five steps to achieve a design that reduces the energy consumption by at least 50%. First, the driving force diagram is generated for the binary pair that represents the primary separation. The driving force exploits the difference in properties that is utilized in that separation process, such as the difference in volatility for distillation (Bek-Pedersen and Gani, 2004). Then, in the next step, with the help of a database of reboiler and condenser duties for various product purities, the energy required to obtain the target purity and the intermediate purity (the purity entering the

membrane) are determined. In the third step, the potential energy savings are calculated (Tula et al., 2017). The hybrid process is then simulated in the fourth step. This determines the actual energy savings of the hybrid process. Finally, the design of the membrane process, area and cost, is performed. The result is the optimal configuration of the hybrid separation along with the potential energy saving and capital and operating costs.

3.5 Methods and tools

Over the course of the three stages, there are methods and tools that are used which are shared by all or some of the stages. An overview of all the tools, including where they are used and their function, is listed in Table 3.4 (adapted from (Bertran et al., 2017)). In addition to those that have been described previously in Sections 3.2 - 3.4, and their subsections, simulation tools and analysis tools are described in Sections 3.5.1 and 3.5.2.

3.5.1 Simulation tools

In order to perform the rigorous design and simulation in stages 2 and 3, simulation tools are needed. These tools contain detailed property models, model equations (mass balance and energy balances), equipment models and powerful calculation tools, that are used to simulate the process and provide the necessary design information. Tools such as AspenPlus (AspenPlus, 2016) and SIMSCI ProII (SimSci, 2016) are used to achieve this.

3.5.2 Analysis tools

In order to determine the sustainability of the processing route and designed processes across the three stages, analysis tools are implemented. There are various types of tools that are used. They fall into three categories: economic, sustainability, and life cycle assessment. Economic analysis tools include the tool ECON (Saengwirun, 2011). In this tool, or similarly in economic tools provided by simulation software, the economic parameters are calculated via the Guthrie Method (Seider et al., 2008). These economic parameters include operating costs (OPEX), capital costs (CAPEX), return on investment (ROI), and production costs. These indicators provide an insight into the economic feasibility of the CCU processes. Then, the tool SustainPro (Carvalho et al., 2013) can be used to analyze the process in terms of sustainability. In this tool, factors such as energy waste consumption (EWC) and material value added (MVA) are used to determine the “hot spots” or areas of the

process which can be improved. And finally, life cycle analyses are performed with the tool LCSoft (Kalakul et al., 2014), which applies ReCiPe LCI to transform the results from the inventories to the indicators (Goedkoop et al., 2008). Through the use of inventories and process stream and equipment data, it is possible to assess the process acording to sustainability indicators, especially carbon footprint.

3.5.3 Evaluation criteria

The processes are all analyzed for $NetCO_2$ as a means for comparison across the stages. $NetCO_2$ is defined in Equation 3.41.

$$NetCO_2 = Indirect_{CO_2} - Utilized_{CO_2} \tag{3.41}$$

This criterion must be considered in evaluating an application scenario during the second stage. When the right hand side of Equations 3.41 is negative, the amount of CO_2 that is utilized by the process is greater than the amount that is generated making it a CO_2 reducing process. However, when the $NetCO_2$ emission for a process alternative is positive, it should not be rejected, rather, the new conversion process should be compared with existing conventional processes. If the emissions are lower in the generated process alternative, then a reduction of CO_2 emission has been achieved. In other words, a relative reduction with respect to the level of business as usual (BAU) has been achieved.

While the CO_2 emission criterion has the highest priority in determining optimal CO_2 utilization processes, other factors, such as, economic indicators and sustainability factors, are also considered. The processes are analyzed for sustainability according to the IChemE sustainability metrics (Cuéllar-Franca and Azapagic, 2015). That is, the streams entering and leaving the process are analyzed for toxicity, environmental impact (including the global warming potential (GWP)), and the economic feasibility (via the operating costs, capital investment, payback period, and utility requirements). The operating costs and investments indicate to a company how much investment will be needed. Additionally, the utility requirements are an indicator of sustainability because utilities are often associated with negative environmental impact.

Table 3.4. The tools used in the framework, including a description and function (adapted from Bertran et al. (2017)).

Name	Type	Step	Description	Function
ProCAMD	In-house	RPS Step b	Program interface for Computer-Aided Molecular Design	Generation of the reaction products for RPS
ProCARPS	In-house	RPS Steps c and d	Program interface for Computer-Aided Reaction Path Synthesis	Generation of all, including the thermodynamically feasible, reaction paths from carbon dioxide to the products in RPS
RPS Database	In-house	RPS Steps a-g	Storage system of all the information and results of reaction path synthesis (RPS)	RPS data storage/retrieval
Superstructure Database	In-house	1.2 and 1.3	Especially structured system of storage for all the information involved in superstructure generation and solution	Synthesis data storage/retrieval
Super-O	In-house	1.2 and 1.3	Interface for formulation and solution of superstructure optimization problems	User guidance through the formulation and solution of synthesis problems of different kinds
GAMS	External	1.3	Modeling system for mathematical programming and optimization	Solution of the optimization problem
AspenPlus or ProII	External	2.1, 2.2 and Stage 3	Rigorous simulation programs that are used to in the detailed design	Provide base-case, optimize and innovative detailed design with equipment design and stream tables
SustainPro	In-house	2.3 and Stage 3	Tool for the sustainability analysis	Determine sustainability indicators and hot spots or targets for improvement
ECON	In-house	2.3 and Stage 3	Tool for the economic analysis	Determine economic parameters and hot spots or targets for improvement
LCSoft	In-house	2.3 and Stage 3	Tool for life cycle assessment (LCA)	Determine carbon footprint and other sustainability indicators along with hot spots and targets for improvement
Process Intensification	In-house	Stage 3	A method that allows for systematic process intensification based on phenomena	Development of intensified process alternatives
Simulation library	In-house	Stages 2 and 3	Library of all the simulations accross the stages	Storage/reuse of simulations

Chapter 4

Application

Summary and significance:

In this chapter, the application of the framework is presented. The three-stage framework is applied to the design of sustainable carbon dioxide capture and conversion processes. In the first stage, the superstructure is generated and optimized. Through the use of reaction path synthesis, a complete list of conversion reactions and products is obtained. The optimization is performed for seven scenarios, considering the influence of the objective function, reaction conversion, location, product demand and prices. From the first stage, dimethyl ether and dimethyl carbonate via methanol are determined to be the most promising products via different conversion routes. The optimal processes are then considered in Stage 2. The design and analysis of the different processes considered is presented and the targets for improvement are obtained. More sustainable processes, which address these targets, are achieved in Stage 3, by the application of intensification and hybrid methods. Through the use of a hybrid distillation-membrane concept, the methanol part of the processes is improved and through the use of reactive distillation, the dimethyl carbonate process can be intensified. Each of the Stages and the results will be discussed to analyze the results.

Outline:

The framework presented in Chapter 3 is applied to the sustainable design of carbon dioxide capture and utilization processes. The goal is to convert carbon dioxide from flue gas to value-added chemicals and thereby reduce emissions. The 3-stage approach is used to first determine the optimal processing route, then design the process in detail and, finally, provide more sustainable design alternatives.

4.1 Stage 1: Synthesis

In the first stage, the goal is to find the optimal processing route(s) taking carbon dioxide captured from a coal-fired power plant to a value-added product. A coal-fired power plant is selected as the emission source as these emissions represent almost 30% of global emissions and therefore addressing them can provide a significant impact. This is achieved by applying the steps in the framework, which apply the superstructure-based method.

4.1.1 Step 1.1: problem definition

First, the objectives of the synthesis problem are defined. The goal of the synthesis stage is to find the best sustainable process to produce value-added products from carbon dioxide. A single feedstock from the database is considered, which is carbon dioxide captured from flue gas from a coal-fired power plant. The objective function is to maximize the profit with an additional ranking based on $NetCO_2$ (see Equation 3.41). In this case, the location of the conversion process is considered to be the same as the location of the capture process located in the United States. The reaction pathways yielding potential products are not known beforehand, so they need to be generated systematically using reaction path synthesis (RPS), as described in Section 3.2.3 and the results are presented in Section 4.1.2.

The objective function for maximizing profit is defined by Equation 4.1, which is based on the objective function in Section 3.2, however transportation and waste costs are not considered.

$$F_{obj} = \max Z = S^{PROD} - C^{RAW} - C^{CHEM} - C^{UT} - \frac{C^{CAP}}{\tau} \tag{4.1}$$

Here, S^{PROD} is the product sales, C^{RAW} is the cost of raw materials, C^{CHEM} is the cost of added chemicals, C^{UT} is the cost of utilities, and C^{CAP} is the capital cost, which is a function of the project lifetime τ. These elements are defined by Equations 3.3, 3.4, 3.5, 3.6 and 3.9, which are function of the parameters for the product prices P^{PROD}, raw material prices P^{RAW}, chemical prices P^{CHEM} and utility prices P^{UT}, respectively. This objective function is constrained by the equality and

inequality constraints that are defined in the Section 3.2, which include constraints on the mass balances (with the product amount F^{PROD}, feedstock amount F^{RAW} and the reaction conversion parameter θ included in these constraints).

4.1.2 Reaction path synthesis (RPS)

The reaction pathways from carbon dioxide yielding value-added products are generated by the seven step method for reaction path synthesis (RPS). Step a translates the objectives of the synthesis problem (see Section 4.1.1) to constraints and objectives for the RPS. As the goal is to design sustainable carbon dioxide capture and conversion processes, the products that are produced should also fulfill environmental criteria (non-toxic, not harmful to animals and humans, etc.). This is translated into the limits on the constraints for the computer-aided molecular design problem (CAMD) by limiting chain length, restricting the number of functional groups, and considering only hydrogen, oxygen and carbon atoms. In Step b, a list of over 100 products is generated (see a detailed list in Appendix B.2 Table B.10). Step c is applied to generate a list of over 2000 one or two stage reactions ($A+B \leftrightarrow C(+D)$ and $A+B \leftrightarrow E(+F)$; $E+G \leftrightarrow C(+D)$) converting carbon dioxide, that are chemically feasible. This is reduced to over 100 thermodynamically feasible reactions in Step d. These reactions are linked, in Step e, to form a reaction tree, an excerpt of which is shown in Figure 4.1 and the entire reaction tree is shown in Appendix B.2 Figures B.1 and B.2. In Step f, the result of the literature search is a list of 37 reactions with kinetic information (see a complete list in Appendix B.2 Table B.11). Finally, in Step g, these 37 reactions are transferred to the superstructure database. These reactions produce 13 products, which are listed in Table 4.1. These products are used as the products for the superstructure.

4.1.3 Step 1.2: superstructure generation and data collection

The problem has been defined, in terms of the objective function, feedstock and location, in Step 1.1. Then, the desired products are determined by reaction path synthesis (Table 4.1). The superstructure is generated by linking the feedstock and products with the appropriate processing steps and then connecting the appropriate intervals. This is done by using the database with the stored information on the intervals and connections. The resulting superstructure is shown in Figure 4.2.

4.1.3.1 Scenarios

For the generated superstructure, there are different scenarios that are considered in the optimization to determine the optimal route(s) and the influential factors

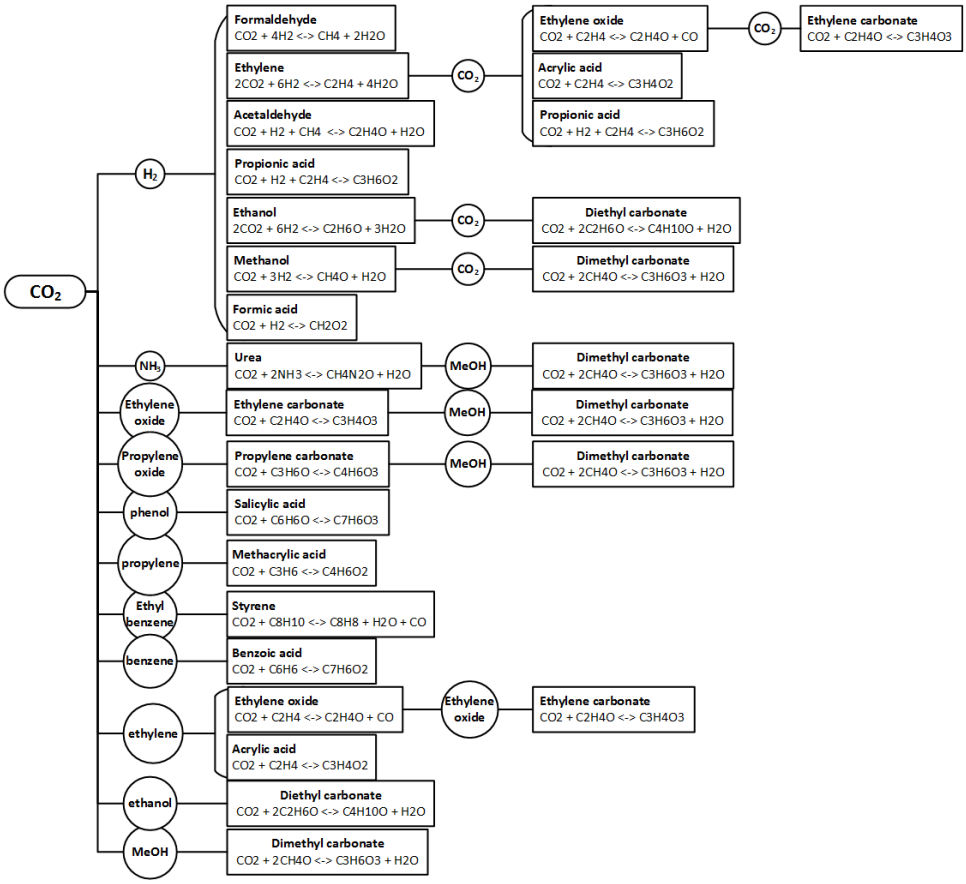

Figure 4.1. An excerpt of the reaction tree generated in Step e of reaction path synthesis.

in the optimization. These scenarios consider different elements in the objective function from Equation 4.1, vary parameter values (prices and reaction conversion θ) or constrain the product amount according to demand (by varying the feedstock amount). All of the scenarios consider the same superstructure and the connections that are present. In addition, the parameter values for mixing (chemical or utility), waste separation and product separation are held constant in all scenarios. The seven scenarios considered are: (1) material costs, (2) operating costs, (3) operating and capital costs, (4) reaction conversion, (5) product price, (6) product demand and (7) location.

Scenarios 1-3 serve to evaluate the most influential parts of the objective function in determining the optimal route. Therefore, the values for the parameters in the model (including the prices P and reaction conversion θ) are fixed, while the components of the objective function that are considered vary. In Scenario 1,

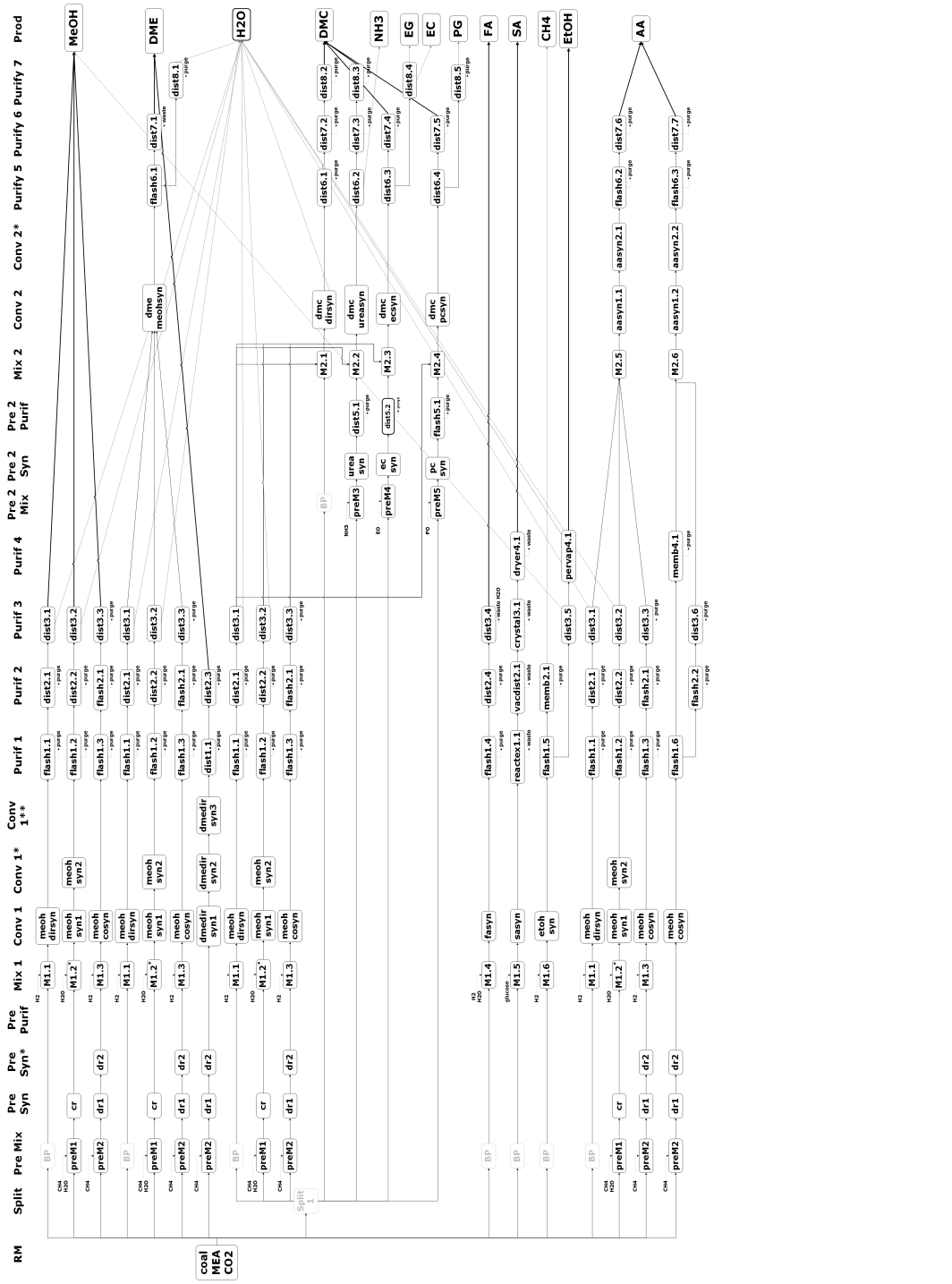

Figure 4.2. The generated superstructure from captured carbon dioxide to value-added products.

Table 4.1. The products and by-products from the reactions that are transferred to the Superstructure database in Step g of reaction path synthesis.

Product	Number of routes
Methanol	3
Dimethyl ether	4
Succinic acid	1
Acetic acid	4
Dimethyl carbonate	4
Ethanol	1
Formic acid	1
Ethylene carbonate (by-product)	
Ethylene glycol (by-product)	
Propylene carbonate (by-product)	
Propylene glycol (by-product)	
Water (by-product)	
Methane (by-product)	

the objective function is a maximization of sales minus material prices, as the sales prices S^{PROD}, raw material costs C^{RAW} and chemical costs C^{CHEM} are considered. Scenario 2 additionally includes the utility cost C^{UT} in the objective function, which means that the result for the objective function is the maximization of sales minus operating costs. Scenario 3 considers the complete objective function described in Equation 4.1, as it also includes the capital cost C^{CAP}.

In Scenarios 4-7, the effect of varying prices, reaction conversion or product amount based on demand on the optimal route(s) is evaluated. All these scenarios consider the objective function for profit shown in Equation 4.1. In Scenario 4, the reaction conversion θ is varied, while all other model parameters remain fixed, to evaluate the potential for routes given new catalysts. For Scenario 5, the product price P^{PROD}, which is present in product sales S^{PROD} in the objective function, is varied to evaluate the influence of fluctuations in prices on the optimal route. Scenario 6 evaluates the influence of the product demand on the optimal routes by varying the feedstock amount F^{RAW}, thereby limiting the product amount F^{PROD} accordingly. In Scenario 7, the different locations are considered by varying the chemical P^{CHEM} and/or utility prices P^{UT}, which are the parameters in the cost of chemicals C^{CHEM} and cost of utilities C^{UT} in the objective function.

These scenarios first evaluate the dominating element of the objective function (Equation 4.1), by considering different elements of it. Then, while optimizing with the same objective function, the influence of prices and reaction conversions is investigated, as prices are variable and the reaction conversion is an important element of carbon dioxide capture and conversion processes. Finally, the demand is considered as this has an impact on the size of the application of the processing

route and the amount of carbon dioxide that can be reduced. An overview of these scenarios and the parameters that are considered or varied are listed in Table 4.2.

Table 4.2. The different scenarios considered in this work.

Scenario	1	2	3	4	5	6	7
Name	Material costs	Operating costs	Operating & capital costs	Reaction conversion	Product price	Product demand	Location
Reaction conversion	x	x	x	varied	x	x	x
Feedstock Amount	x	x	x	x	x	varied	x
Product Amount	x	x	x	x	x	varied	x
Feedstock Price	x	x	x	x	x	x	x
Product Price	x	x	x	x	varied	x	x
Chemical Price	x	x	x	x	x	x	varied
Utility Price		x	x	x	x	x	varied
Capital Cost			x	x	x	x	x

4.1.4 Step 1.3: solution of the optimization problem

The superstructure generated in Step 1.2 is solved according to the seven different scenarios. This is facilitated by the use of the software interface, Super-O. All the data for the superstructure and the parameters is stored as an excel input file. This input file defines all the parameters needed by the GAMS model. Using GAMS, the optimization problem is solved and generates an excel output file. Each scenario therefore has an input file and an output file that store the parameter values and can therefore be stored and used to resolve the problem at any point in time. Table 4.3 lists the properties of the superstructure, which is the same for all scenarios, and the properties of the model.

4.1.4.1 Scenarios 1-3

For the first three scenarios, the different objective function scenarios all results in the same optimal processing route. The optimal route is the production of dimethyl ether (DME) via combined reforming, which is shown in Figure 4.3. Table 4.4 lists the objective function value, the overall capital cost (CAPEX) for the 10 year project

Table 4.3. The statistics of the superstructure and the mathematical model for the generated superstructure.

Superstructure	No. of feedstock	1
	No. of products	12
	No. of steps	24
	No. of intervals	167
Mathematical model	No. of equations	3150683
	No. of discrete variables	366
	Solution time (s)	15

time, the operating costs (OPEX), the product sales, the raw material cost, the utility cost, the chemical costs, the NetCO_2, and the global CO_2 reduction potential per year.

Table 4.4. The important results for the solutions of Scenarios 1-3, 4 and 7.

Scenario	**1**	**2**	**3**	**4**	**7**
Route	**DME via MeOH from combined reforming**	**DME via MeOH from combined reforming**	**DME via MeOH from combined reforming**	**Succinic acid**	**Succinic acid**
Objective function (MM USD/y)	276.0	246.5	202.9	220.8	201.6
CAPEX (MM USD)	0.0	0.0	653.8	582.1	582.1
OPEX (MM USD/y)	96.5	126.0	126.0	553.8	576.3
Sales (MM USD/y)	372.5	372.5	372.5	813.4	813.4
Raw material cost (M USD/y)	21.4	21.4	21.4	21.4	21.4
Utility cost (MM USD/y)	0.0	29.5	29.5	12.1	13.3
Chemical cost (MM USD/y)	96.5	96.5	96.5	541.7	541.7
NetCO2 ($kg_{CO_{2,eq}}/kg_{Prod}$)	-0.43	0.07	0.07	0.03	0.03
Global reduction potential (MM $t_{CO_{2,eq}}$/y)	-33.1	-9.8	-9.8	0.002	0.002

4.1.4.2 Scenario 4

In the fourth scenario, the reaction conversions of the reactions are manipulated (from the current reaction conversion to a maximum equilibrium reaction conversion) to consider the possibility of higher reaction conversion as a result of improved catalysts. As a result of changing reaction conversion, however, only the processing

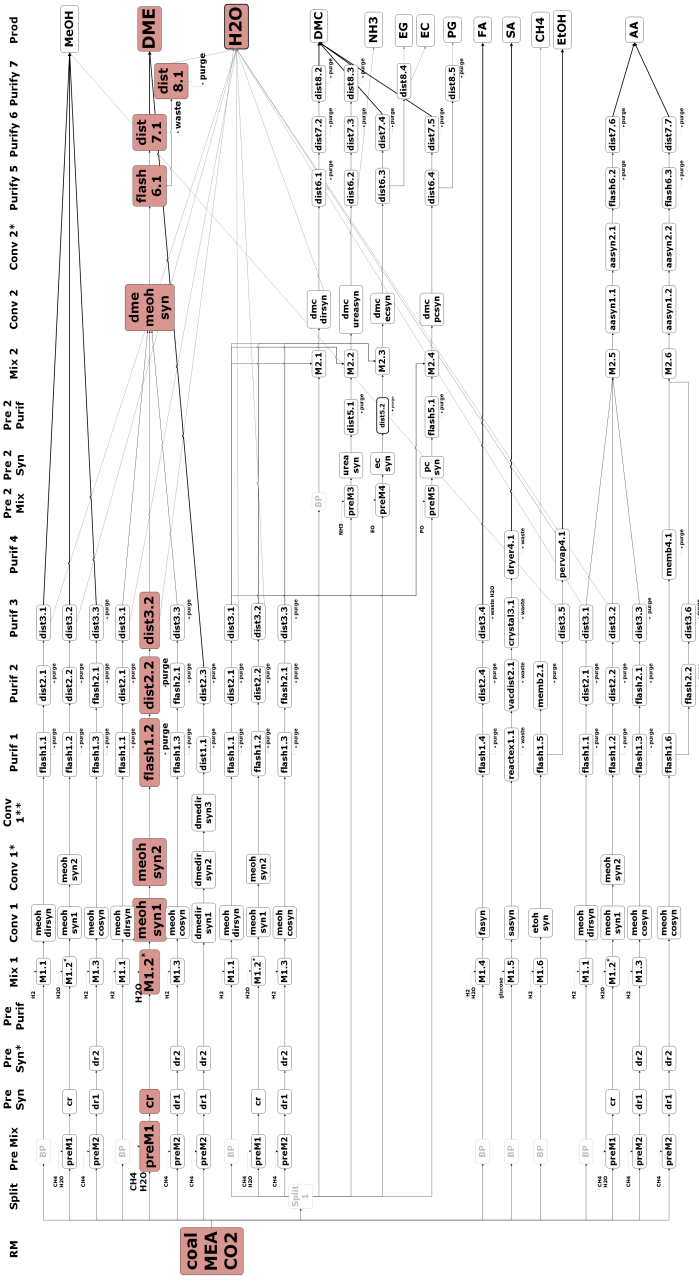

Figure 4.3. The superstructure with the optimal route for Scenario 1, 2 and 3 highlighted in red.

route to succinic acid is improved enough to be more optimal. This route is shown by the green route in Figure 4.4 and Table 4.4 lists the solution results (the objective function, the overall capital cost (CAPEX) for the 10 year project time, the operating costs (OPEX), the product sales, the raw material cost, the utility cost, the chemical cost, the NetCO_2, and the global CO_2 reduction potential per year).

4.1.4.3 Scenario 5

The fifth scenario varies the product price to determine the price variation needed for the different products to be optimal. By varying the product prices individually, it is determined that the production of methanol, dimethyl carbonate, succinic acid and acetic acid would require the smallest increase in price. The calculated prices and the corresponding increase from the current prices are listed in Table 4.5.

Table 4.5. List of the price changes needed for the products to be selected as the optimal route according to the economic objective function.

Product	**Route**	**Price needed (USD/kg)**	**increase in price**
Methanol	via combined reforming	0.68	42%
Dimethyl ether (DME)	via MeOH from combined reforming	0.97	0%
Formic acid	via hydrogenation	15.10	1941%
Succinic Acid	via glucose fermentation	1.98	10%
Acetic acid	via carbonylation of MeOH from combined reforming	1.60	119%
Dimethyl carbonate	via EC and MeOH from combined reforming	1.60	60%

The routes for methanol, acetic acid, succinic acid and dimethyl carbonate, which require the smallest changes in price, are shown in Figure 4.4. The important solution results, which describe the differences in the optimal routes at the increased product prices, are listed in Table 4.6, with the objective function maximizing profit according to Equation 4.1.

4.1.4.4 Scenario 6

In Scenario 6, the product amount is varied by varying the feedstock amount, while considering the objective function maximizing profit (see Equation 4.1). By adjusting the amount of carbon dioxide used to produce the different products, to account for the demand of the products, the amount of carbon dioxide that can be reduced changes. When the demand is considered, the objective function (profit), NetCO_2 and the global CO_2 reduction vary for each route. In Figure 4.5, the results

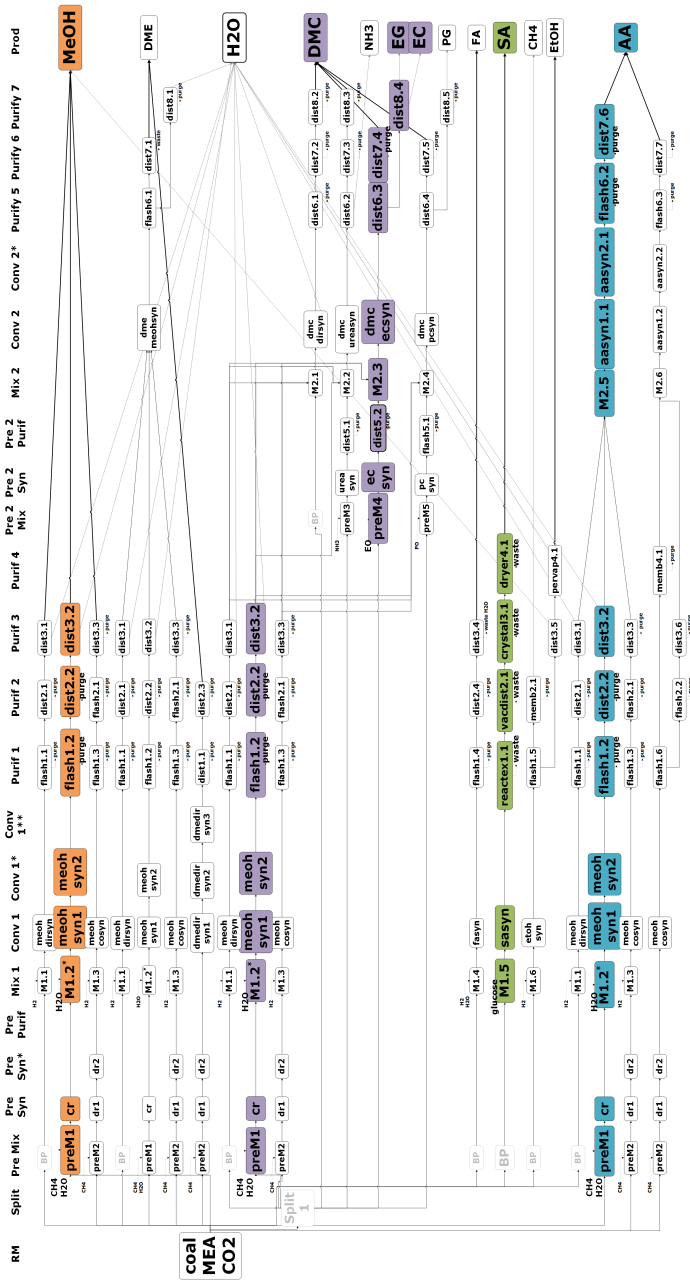

Figure 4.4. The superstructure in which the optimal route for Scenario 4 and 7 (succinic acid) is highlighted in green. Then, the routes for Scenario 5 are shown: methanol in orange, dimethyl carbonate in purple, succinic acid in green and acetic acid in blue. These routes require the smallest price changes to be deemed economically optimal.

Table 4.6. The solution results for the different routes in Scenario 5.

Route	**MeOH**	**DMC**	**Succinic acid**	**Acetic acid**
Objective function (MM USD/y)	158.3	172.8	158.2	157.8
CAPEX (MM USD)	306.9	254.7	279.6	403.9
OPEX (MM USD/y)	93.0	245.8	395.4	342.6
Sales (MM USD/y)	282.0	444.0	581.5	540.8
Raw material cost (M USD/y)	5.3	5.3	5.3	5.3
Utility cost (MM USD/y)	20.6	14.9	8.1	25.1
Chemical cost (MM USD/y)	72.4	230.8	387.3	317.6
$NetCO_2$ ($kg_{CO_{2,eq}}/kg_{prod}$)	0.20	0.04	0.03	0.21
Global reduction potential (MM $t_{CO_{2,eq}}$/y)	-19.7	-1.2	0.002	-0.37

for these three values are shown, revealing that there is a trade-off between the profit and the amount of carbon dioxide that can be reduced.

The most promising routes, which have the highest profit with reduction potential, methanol (MeOH), dimethyl ether (DME) and dimethyl carbonate (DMC), are highlighted in Figure 4.6. The most important solution results for these routes (objective function, $NetCO_2$ and global reduction potential) are listed in Table 4.7.

4.1.4.5 Scenario 7

The seventh scenario considers different locations by varying the chemical and utility prices by factors, considering the objective function in Equation 4.1. Of the differences tested within a 10% range, only an increase by 10% in the utility prices results in another solution. If the utility prices are increased by 10%, the optimal route produces succinic acid. This route is shown by the green route in Figure 4.4 and the results of the objective function, etc. are listed in Table 4.4.

4.1.5 Discussion Stage 1 results

Stage 1 of the framework is applied to determine the optimal processing route(s) and products from a single feedstock (carbon dioxide from a coal-fired power plant) to a value added product. After Step 1.1, reaction path synthesis is used to generate all the reaction pathways to convert carbon dioxide to value-added products. These reactions define the products that are included in the superstructure. The superstructure database is then used to generate the superstructure of all the alternatives for Stage 1. This superstructure contains 26 processing routes to 13 products and by-products. The optimization is performed considering seven scenarios.

The Scenarios 1, 2 and 3 are used to determine if material costs, utility costs

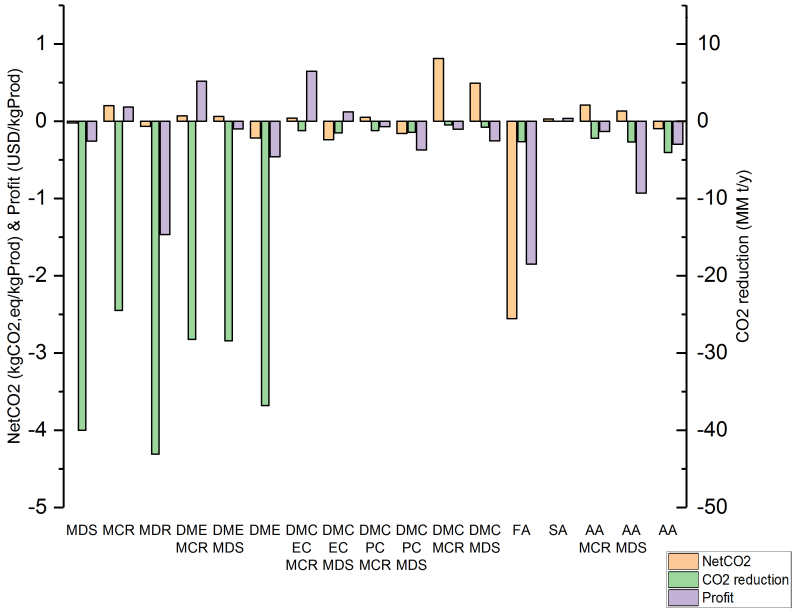

Figure 4.5. The results for the $NetCO_2$, profit and CO_2 reduction for the different processing routes in Scenario 6. Here, MDS is methanol direct synthesis, MCR is methanol via combined reforming, MDR is methanol via dry reforming, DME is dimethyl ether via direct synthesis, DME MCR and DME MDS are the two dimethyl ether routes via methanol, DMC EC is dimethyl ether via ethylene carbonate, DMC PC is dimethyl ether via propylene carbonate, DMC MCR and DMC MDS are the two direct dimethyl carbonate routes from methanol, FA is formic acid, SA is succinic acid, AA is acetic acid with the use of a membrane after the dry reforming, and AA MCR and AA MDS are the two acetic acid routes via methanol.

or capital costs dominate the solution. In these scenarios, with the results listed in Table 4.4, the same process is optimal in each case. The production of dimethyl ether via methanol synthesis from combined reforming syngas, considering material, utility and capital costs is optimal. In addition, as the breakdown of costs in the table indicates, the chemical costs dominate the optimal route. This indicates that if the prices of the chemicals were to change, the route might change as well.

Then in Scenario 4, the reaction conversion is varied for the reactions. As carbon dioxide capture and conversion processes are still in early stages of development, new catalysts or reactor configurations could be developed which improve the reaction conversions. Therefore, it is of interest to see if this improved reaction conversion alone would influence the optimal route. However, only one product,

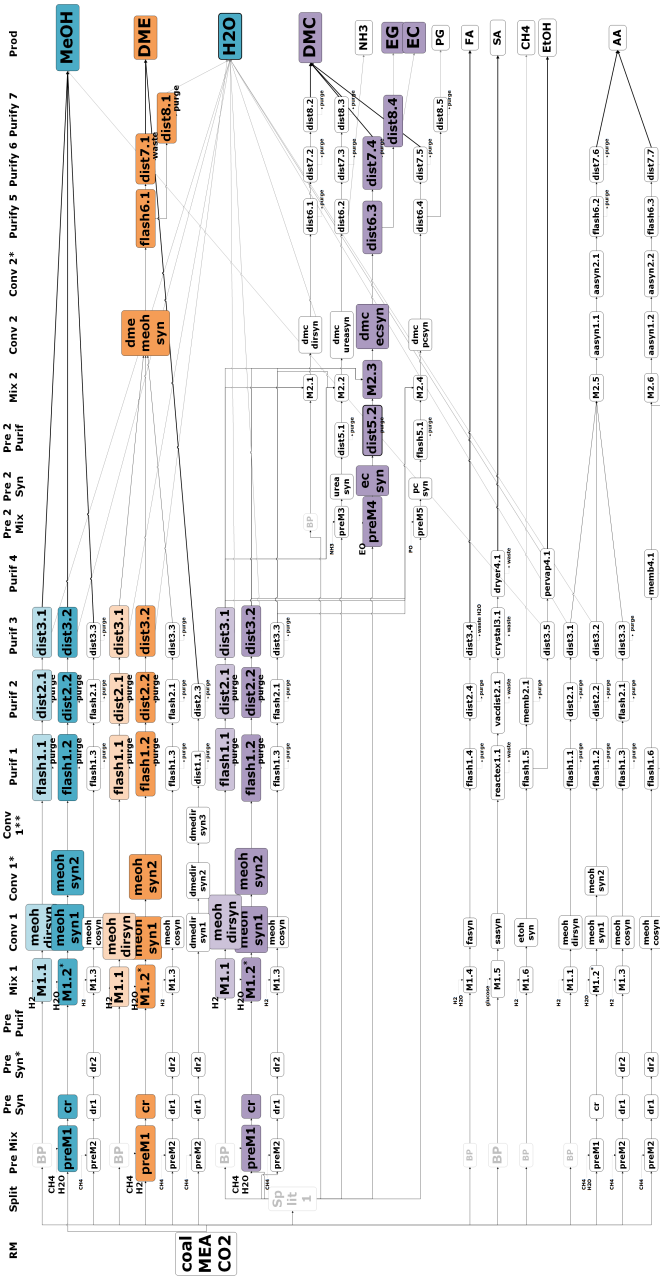

Figure 4.6. The superstructure in which the optimal routes from Scenario 6 are highlighted; the two optimal routes for methanol are shown in blue, the two optimal routes for dimethyl ether are shown in red and the two optimal routes for dimethyl carbonate are shown in purple.

Table 4.7. The results for the different routes in Scenario 6.

Route	MeOH via combined reforming	MeOH via direct hydrogenation	DME via MeOH from combined reforming	DME via MeOH from direct hydrogenation	DMC via EC and MeOH from combined reforming	DMC via EC and MeOH from direct hydrogenation
Objective function (MM USD/y)	65.2	-16.3	24.9	-2.3	58.6	7.6
Product amount (MM t/y)	0.75	0.75	0.10	0.10	0.10	0.10
CAPEX (MM USD)	370.0	276.5	128.3	97.2	320.8	242.9
OPEX (MM USD/y)	177.9	268.7	59.3	89.6	165.5	224.3
Sales (MM USD/y)	280.0	280.0	97.0	97.0	256.2	256.2
Raw material cost (M USD/y)	9.7	9.7	1.9	1.9	3.8	3.8
Utility cost (MM USD/y)	37.3	83.0	12.4	27.7	15.8	29.5
Chemical cost (MM USD/y)	130.9	176.0	48.6	63.7	145.9	191.0
NetCO_2 ($kg_{CO_{2,eq}}/kg_{prod}$)	-0.02	0.20	0.07	0.06	0.04	-0.24
Global reduction potential (MM $t_{CO_{2,eq}}$/y)	-40.00	-24.50	-28.25	-28.42	-1.24	-1.52

succinic acid becomes optimal with an improved reaction conversion. This indicates that the reaction conversion alone is generally not the most influential parameter in the optimal solution.

Scenario 5 varies the product price until that product becomes optimal to account for the fluctuating prices as a result of the changing demand and the cost of the typical raw materials in the industrial production. The results of this Scenario show that succinic acid, methanol, dimethyl carbonate and acetic acid need to have their prices increased by 10%, 42%, 60% and 119% respectively. Alternatively, the price of the other products could decrease by these values, while the prices of the

individual products is held constant. These four processes are therefore considered in more detail at these prices. The results (see Table 4.6) show that the profit for these products is similar. However, the dominant element of the objective function varies. For methanol, the sales, chemical cost, utility cost and capital cost are small, with the capital costs dominating the need for the increased price. Dimethyl carbonate, on the other hand, is dominated by the operating costs, particularly chemical costs. Both succinic acid and acetic acid routes have high sales as the products have a higher value. However, they also have the highest chemical costs. While the varying product price in Scenario 5 indicates the influence that the price will have, an analysis of the breakdown of the objective functions, reveals that the chemical costs are dominant for dimethyl carbonate, succinic acid and acetic acid.

Scenario 6 is important as it considers the plant capacity along with the global demand to assess the potential impact of the different routes. In this scenario, the feedstock amount is varied to vary the product amount according to the demand of the products. The results of the profit (per kg_{Prod}), global CO_2 reduction potential and the NetCO_2 are shown in Figure 4.5. This indicates that there is often a trade-off in the carbon dioxide that can be reduced annually and the profit, for the routes. The routes that are most profitable are: (1) dimethyl carbonate via ethylene carbonate and methanol from combined reforming syngas, (2) dimethyl ether via methanol from combined reforming syngas, and (3) methanol from combined reforming syngas. However, the reduction potential of these routes is increased when the methanol is synthesized via direct hydrogenation. Also, dimethyl carbonate, while the most profitable has the smallest impact of these three routes due to the small demand. The results in Table 4.7 indicate that the operating cost for the methanol synthesis via direct hydrogenation are higher due to the higher price of raw materials and the increased utilities. In addition, the dimethyl carbonate processes have the highest operating costs, but for the smaller production amount compared to methanol, the capital costs are lower. The dimethyl ether process has the lowest capital and operating costs, but also has the lowest sales.

In Scenario 7, the changing of the utility prices is considered to be higher or lower by 10%. This resulted in the selection of succinic acid, when the utility price was increased by 10%. The breakdown of the objective function results are presented in Table 4.4. As the objective function is close enough to that for dimethyl ether via methanol from combined reforming syngas and the utility costs are significantly lower, the increase in the utility costs results in succinic acid being optimal.

The scenarios show that the product price and the product demand have an influence on the optimal route and the carbon dioxide that can be reduced. Based

on the potential for carbon dioxide reduction and profit, four routes, which use methanol, are selected: (1) dimethyl ether via methanol from combined reforming, (2) dimethyl ether via methanol from direct hydrogenation, (3) dimethyl carbonate via ethylene carbonate and methanol from combined reforming, and (4) dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation.

4.2 Stage 2: Design

Due to the trade-offs between the reduction of CO_2 and the profit, the optimal processes are limited. The four promising routes involve the production of dimethyl ether (DME) and dimethyl carbonate (DMC). The four routes are: (1) the production of dimethyl ether via methanol from combined reforming, which is the optimal route in Scenarios 1-3 (see Section 4.1.4.1), (2) the production of dimethyl ether via methanol from direct hydrogenation as this provides a higher reduction of carbon dioxide compared to route 1 (see Scenario 6 results in Section 4.1.4.4), (3) the production of dimethyl carbonate via ethylene carbonate and methanol from combined reforming, which is the most profitable (per kilogram of product) from Scenario 6 (see Section 4.1.4.4), and (4) the production of dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation as this also provides an increased reduction of carbon dioxide compared to route 2 (see Scenario 6 results in Section 4.1.4.4). The design and analysis of these four processes is performed in Stage 2. All processes are designed to produce 0.1 million tons of product per year. Additional details for both processes can be found in Appendix D.

4.2.1 CCU: Dimethyl ether (DME) production

The two routes for dimethyl ether (DME) production (shown in red in Figure 4.6) are designed according to the flowsheet shown in Figure 4.7. The flow diagrams are broken down into three parts: the carbon capture process, methanol synthesis and dimethyl ether synthesis.

4.2.1.1 Step 2.1: detailed design and simulation

The first step in this stage, is the detailed design and simulation according to the framework. From Stage 1, the process flow diagram along with material balances is provided. With the use of literature (for information on catalysts and operating conditions) and design principles (distillation column design, etc.), the equipment is designed in detail (for example sizing) and then the process is simulated, in this case using ProII.

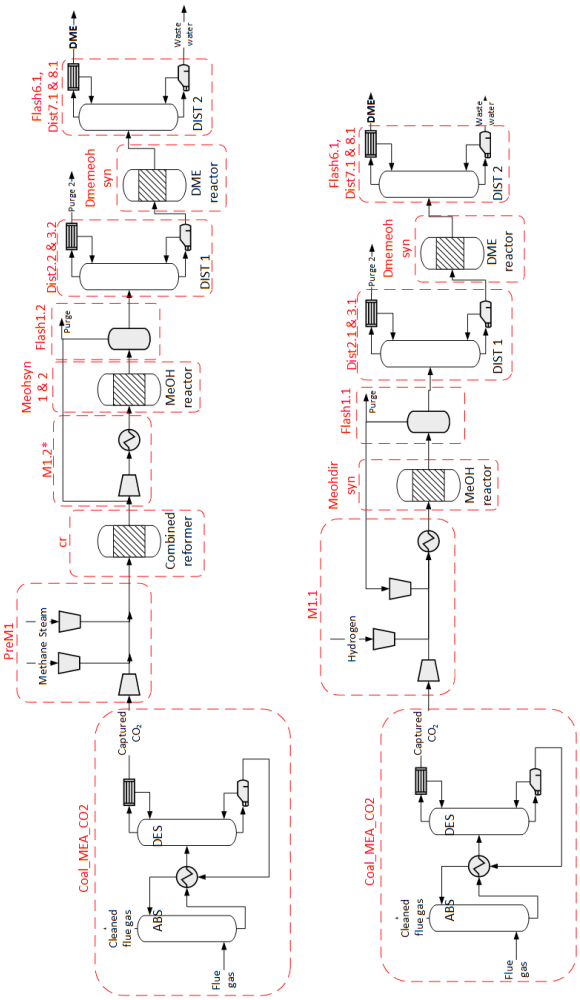

Figure 4.7. Process flow diagram of the carbon dioxide capture and conversion processes to dimethyl ether (DME) via methanol from direct hydrogenation (right) and combined reforming of methane (left).

Carbon capture The carbon dioxide capture process is the first part of the flow diagram. It is a monoethyl amine (MEA) absorption/desorption process. The capture process was previously optimized to reduce the reboiler duty in the desorption column (Fjellerup, 2015) by reducing the purity of the outlet carbon dioxide stream from 99.9 mol% to 97.2 mol%, realizing a tenfold reduction in utility consumption. In this section of the process, the thermodynamic model for amines is used. (See Appendix Section D.1 for additional details.)

Methanol synthesis There are two methanol synthesis routes considered, methanol from combined reforming syngas and methanol from direct hydrogenation. Combined reforming uses the captured carbon dioxide along with methane and steam to produce a syngas with a $2H_2$:1CO ratio. For the combined reforming route, the reforming reaction is modeled using a Gibb's reactor, which minimizes the Gibb's energy in the reactor as there is no kinetic model, at 25 bar and 915°C. The feed to the methanol reactor needs to be compressed. This can be done by a single compressor or by a multi-stage compressor. In this work, a multi-stage compressor is considered. Then, the methanol synthesis reaction is modeled using a Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic model (Bussche and Froment, 1996) at 60 bar and 240°C. This model and the operating conditions are also used to model the methanol synthesis via direct hydrogenation, which reacts the captured carbon dioxide with hydrogen directly to produce methanol. The product from the reactor is first flashed to separate the light gases and then distillation is used, as there is no azeotrope present, to purify the methanol from water before the dimethyl ether synthesis. In the simulation, Soave-Redlich-Kwong is used as the thermodynamic model as it is appropriate for the mixture present and describes the behavior accurately. (See Appendix Sections D.2 and D.3 for additional details.)

Dimethyl ether synthesis The dimethyl ether synthesis uses the methanol to produce dimethyl ether and water. This reaction is described by a LHHW kinetic model (Ng et al., 1999) and the operating conditions are 10 bar and 240°C (Prasertsri et al., 2016). Subsequently, distillation is used to separate the dimethyl ether and the methanol as, again, no azeotropes are present. In the simulation, Soave-Redlich-Kwong is also used as the thermodynamic model as it is appropriate for the mixture present and describes the behavior accurately. (See Appendix Section D.4 for additional details.)

The two integrated dimethyl ether processes are then simulated in ProII and the flowsheets are shown in Figures 4.8 and 4.9. The detailed stream information is provided in Appendix Section D.7.

As the operating conditions for the catalyst have been optimized previously, Step 2.2 is not performed.

4.2.1.2 Step 2.3: analysis

After the simulation is performed, the results are analyzed for economic and environmental parameters. This is done by using the tools ECON (Kalakul et al., 2014) and LCSoft (Kalakul et al., 2014) to obtain the economic and environmental/life cycle impacts, respectively. Using the stream tables and the equipment information

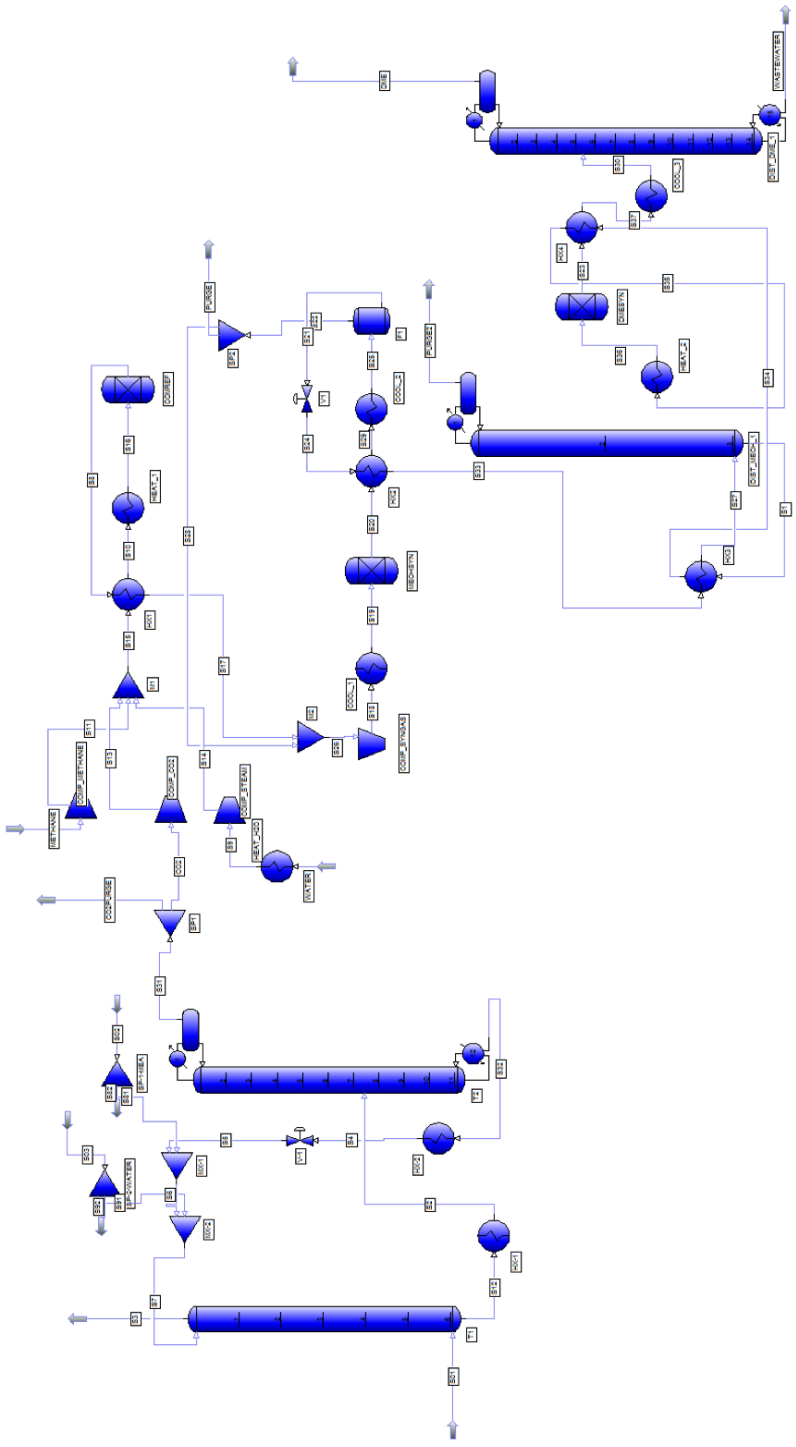

Figure 4.8. ProII flowsheet of the process for the synthesis of dimethyl ether from methanol via combined reforming.

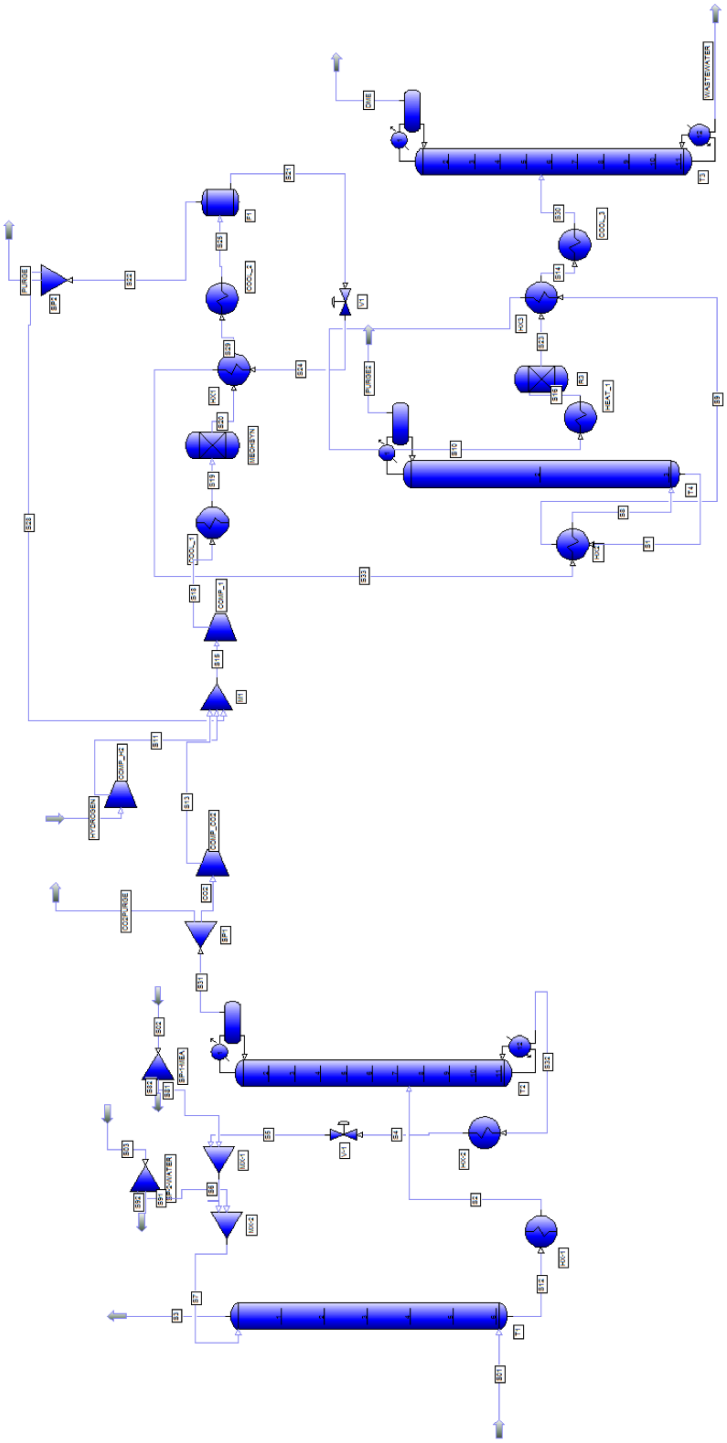

Figure 4.9. ProII flowsheet of the process for the synthesis of dimethyl ether from methanol via direct hydrogenation.

from the design, the economic parameters are calculated. Some of the important results, operating costs, capital costs and production costs, are listed in Table 4.8. In addition, the contributions of the different units of the integrated process to utility costs and capital costs are shown in Figures 4.10, 4.11, 4.12 and 4.13. Then, using the tool LCSoft along with the stream and equipment information, the carbon footprint and other environmental indicators are calculated for the processes. The carbon footprint for each of the units confirms the breakdown of the utility costs shown in Figures 4.17 and 4.18. The entire carbon footprint of the processes combined with the carbon dioxide utilized in the process is used in the calculation of the NetCO_2, which is also listed in Table 4.8.

Table 4.8. Important results from the analysis of the dimethyl ether capture and conversion processes.

	DME with CR MeOH	**DME with direct MeOH**
Capture		
CAPEX (MM USD)	31.1	31.1
OPEX (MM USD/y)	69.4	69.4
Utility cost (MM USD/y)	42.3	42.3
Methanol synthesis		
CAPEX (MM USD)	209.3	257.4
OPEX (MM USD/y)	205.7	233.9
Utility cost (MM USD/y)	23.6	34
Dimethyl ether synthesis		
CAPEX (MM USD)	19.4	19.4
OPEX (MM USD/y)	10.5	10.5
Utility cost (MM USD/y)	5.4	5.4
Integrated process		
CAPEX (MM USD)	259.8	307.9
OPEX (MM USD/y)	285.6	313.8
NetCO2 ($kg_{CO_{2,eq}}/kg_{Prod}$)	0.08	-0.17
Production cost (USD/t)	780	897
Global CO_2 reduction (MM $t_{CO_{2,eq}}$/y)	-9.7	-35.4

From the analysis of the utility costs, it is evident that the capture process, the compression of methane, hydrogen, and carbon dioxide, and the distillation of methanol are the largest contributors. Therefore, these are also the largest contributors to the carbon footprint. The capture process and the conditions have already been optimized to reduce the reboiler duty, which is the high utility consumption, and therefore, this is not targeted for further improvement. The compression cannot be further improved either, as the process design already considers a multi-stage compressor, which decreases the energy consumption but increases the capital costs. The high utility consumption of the methanol distillation, however, has not been previously addressed. Therefore, the reduction of the cost and the utility

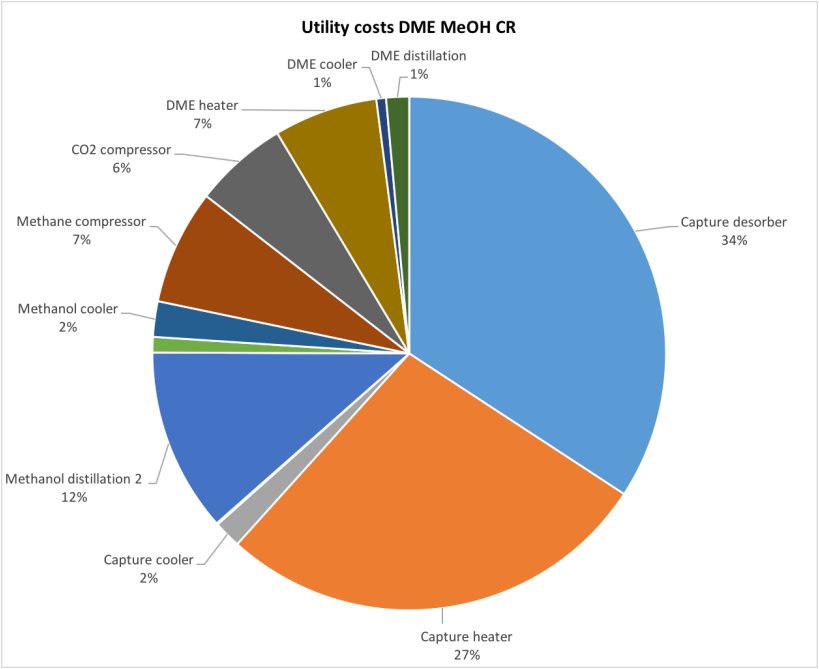

Figure 4.10. The breakdown of the utility costs for the production of dimethyl ether (DME) via methanol (MeOH) from combined reforming (CR).

consumption of the second methanol distillation column is set as the target for improvement.

4.2.2 CCU: Dimethyl carbonate (DMC) production

The two routes for dimethyl carbonate (DMC) production (shown in purple in Figure 4.6) are designed according to the flowsheet shown in Figure 4.14. These processes contain four parts: the capture process, ethylene carbonate synthesis from CO_2, methanol synthesis from CO_2 and dimethyl carbonate production.

4.2.2.1 Step 2.1: detailed design and simulation

Again, from Stage 1, the process flow diagram, along with material balances is provided. With the use of literature and design principles, the equipment is designed in detail and then the process is simulated using ProII. In these two dimethyl carbonate production processes, the carbon dioxide capture part and the methanol synthesis parts remain the same as in the DME processes, therefore only the ethylene carbonate synthesis and dimethyl carbonate synthesis parts are described here.

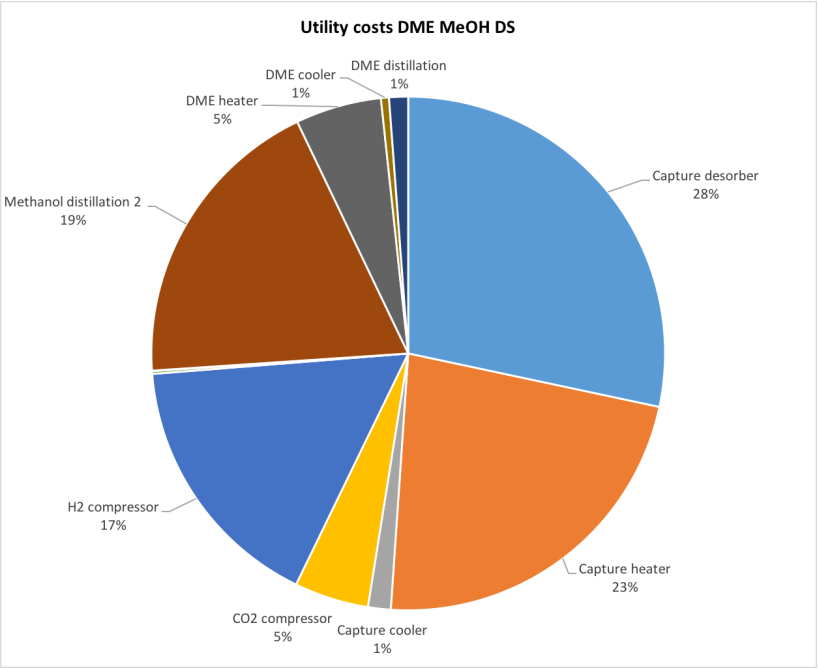

Figure 4.11. The breakdown of the utility costs for the production of dimethyl ether (DME) via methanol (MeOH) from direct synthesis/hydrogenation (DS).

Ethylene carbonate (EC) synthesis Part of the carbon dioxide that is captured is used in the ethylene carbonate synthesis by reacting it with ethylene oxide. This process is performed at elevated pressure, 125 bar, and 110°C (Kongpanna et al., 2015, 2016). The reaction products are separated via distillation as the mixture properties indicate this as suitable. Again, the Soave-Redlich-Kwong is used as the thermodynamic model. (See Appendix Section D.5 for more details.)

Dimethyl carbonate (DMC) synthesis The produced methanol and ethylene carbonate are reacted to produce dimethyl carbonate at 10 bar and 125°C. After the reaction, a series of distillation columns is used to purify the products. The output is a four-component mixture. In the first column, the unreacted methanol and dimethyl carbonate are separated from the unreacted ethylene carbonate and the ethylene glycol. Subsequently, water is added to the mixture, as the ethylene glycol and ethylene carbonate cannot be separated by distillation due to the azeotrope that forms that is not pressure sensitive. This water reacts with the ethylene carbonate to produce ethylene glycol (Fu et al., 2016), which is simply purified by a distillation column as the ethylene carbonate is nearly completely converted. The methanol and dimethyl carbonate also form an azeotrope, however, this is pressure sensitive.

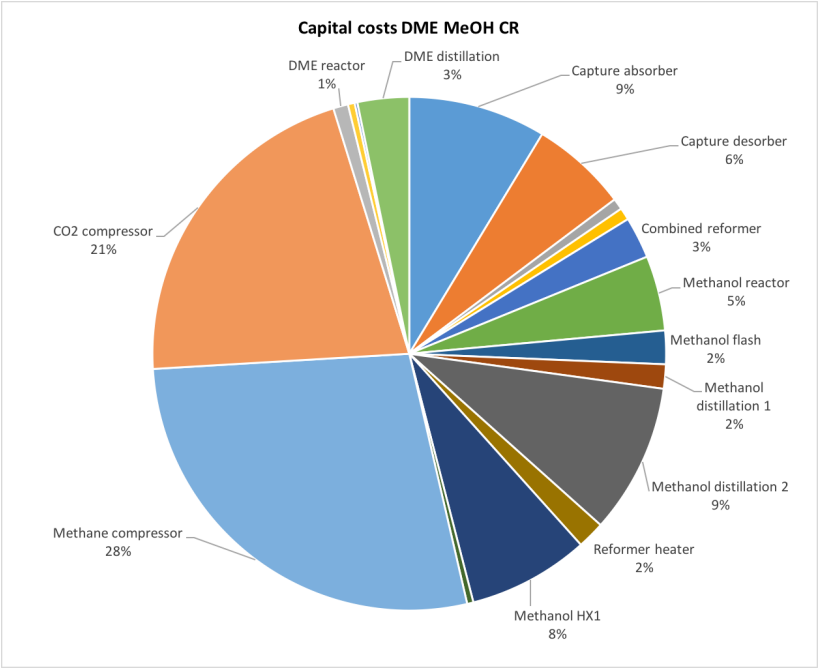

Figure 4.12. The breakdown of the purchase costs for the production of dimethyl ether (DME) via methanol (MeOH) from combined reforming (CR).

By increasing the pressure, the concentration of the mixture shifts to the side of the azeotrope, which allows the separation of purified dimethyl carbonate and azeotropic methanol (95 mol%), which can be recycled. An NRTL model is used with the interaction parameters provided to properly model the interactions in this section of the process (Wang et al., 2010).

Details on the ProII flowsheet and the stream tables are provided in Appendix Section D.8. Again, the flowsheet conditions considered are already optimal for the information available and therefore, Step 2.2 is not performed for these processes.

4.2.2.2 Step 2.3: analysis

Similarly to the dimethyl ether processes, the results are analyzed and the important economic and environmental results for the two processes are listed in Table 4.9. The detailed breakdown of the purchase costs and utility costs are calculated in the analysis and are shown in Figures 4.15, 4.16, 4.17 and 4.18.

From the analysis of these processes, it becomes evident that again the capture process, the compression of methane, hydrogen and carbon dioxide, and the methanol distillation contribute to the utility consumption and costs. In addition,

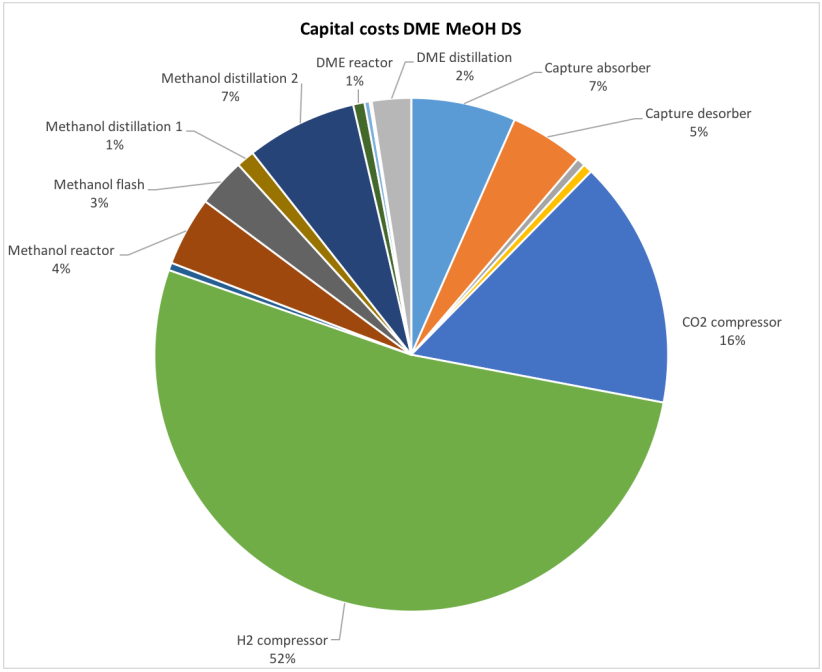

Figure 4.13. The breakdown of the purchase costs for the production of dimethyl ether (DME) via methanol (MeOH) from direct synthesis/hydrogenation (DH).

the dimethyl carbonate downstream separation contributes a large amount to the utility consumption and the costs. Therefore, in addition to the utility consumption of the methanol distillation (as is also the case in the dimethyl ether processes), the high utility consumption of downstream separation of dimethyl carbonate is targeted for improvement (reduction) in Stage 3.

4.2.3 Other processes

In addition to these four processes, there is a simulation library of all the carbon dioxide capture and conversion simulations. These simulations include the individual capture simulations, conversion simulations to a variety of products (including succinic acid and acetic acid), and integrated capture and conversion processes (for example CCU to formic acid and methanol). The complete list of simulations can be found in Appendix B.3 Table B.3.

4.2.4 Discussion Stage 2 results

In Stage 2, the four processing routes which are determined to be optimal from Stage 1 are designed and analyzed. The results of the design and analysis show that

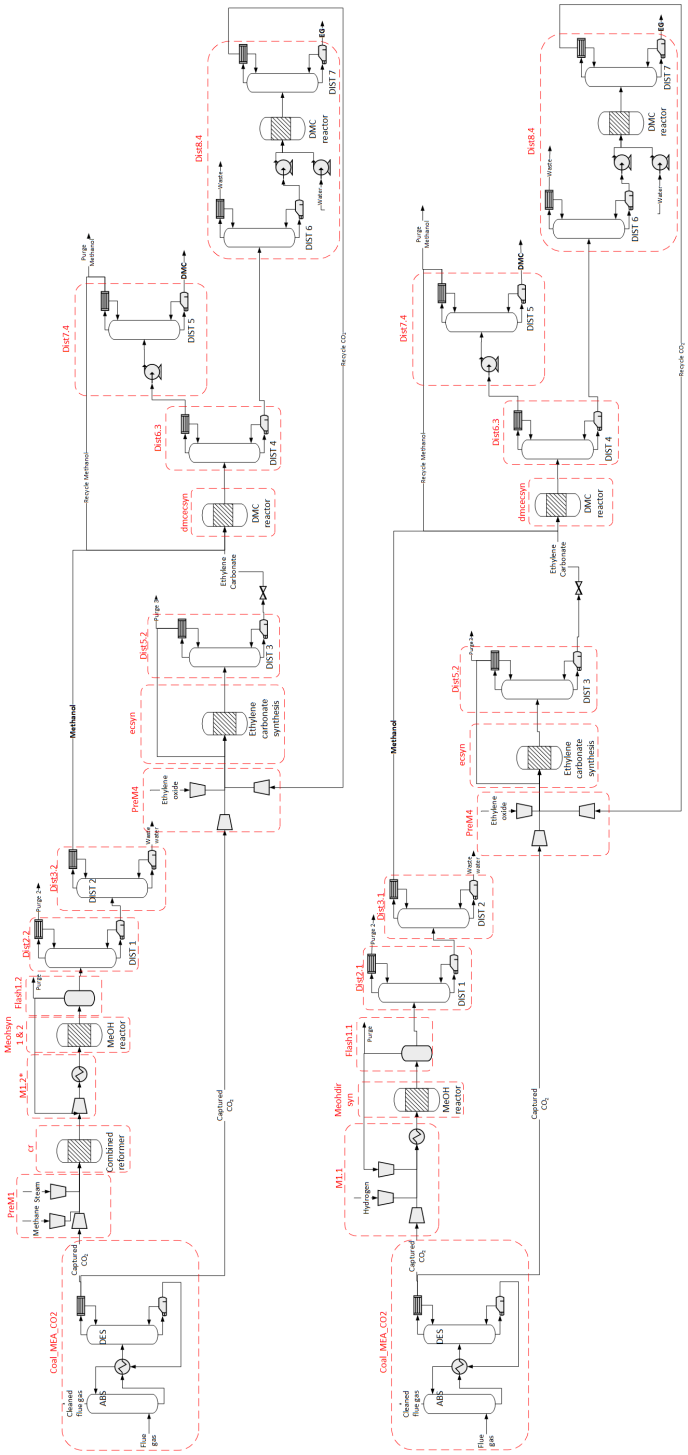

Figure 4.14. Process flow diagram of the carbon dioxide capture and conversion processes to dimethyl carbonate (DMC) via ethylene carbonate (EC) and methanol from direct hydrogenation (right) and combined reforming of methane (left).

Table 4.9. Important results from the analysis of the dimethyl carbonate capture and conversion processes.

	DMC via EC with CR MeOH	**DMC via EC with direct MeOH**
Capture		
CAPEX (MM USD)	31.1	31.1
OPEX (MM USD/y)	69.4	69.4
Utility cost (MM USD/y)	42.3	42.3
Methanol synthesis		
CAPEX (MM USD)	209.3	257.4
OPEX (MM USD/y)	205.7	233.9
Utility cost (MM USD/y)	23.6	34
Ethylene carbonate synthesis		
CAPEX (MM USD)	52	52
OPEX (MM USD/y)	22.5	22.5
Utility cost (MM USD/y)	4.7	4.7
Dimethyl carbonate synthesis		
CAPEX (MM USD)	68	68
OPEX (MM USD/y)	81.8	81.8
Utility cost (MM USD/y)	30	30
Integrated process		
CAPEX (MM USD)	360.4	408.5
OPEX (MM USD/y)	379.4	407.6
NetCO2 ($kg_{CO_{2,eq}}/kg_{Prod}$)	0.04	-0.22
Production cost (USD/t)	1139	1178
Global CO_2 reduction (MM $t_{CO_{2,eq}}$/y)	-1.24	-1.5

carbon dioxide capture and conversion processes to dimethyl ether and dimethyl carbonate can be designed to be carbon dioxide reducing and profitable.

The designed process for dimethyl ether via methanol from combined reforming can globally reduce carbon dioxide, as the $NetCO_2$ is lower than the current industrial process. Industrial methanol synthesis uses a 2-step reforming process with 0.55 kg_{CO_2}/kg_{Prod}. The dimethyl ether synthesis, which uses this methanol, has an industrial $NetCO_2$ of 0.99 kg_{CO_2}/kg_{Prod}. In addition, the process is profitable, as the production costs are lower than the selling price (970 USD per ton dimethyl ether). The dimethyl ether process via methanol from direct hydrogenation, is $NetCO_2$ negative and profitable. However, the profit is lower than the process via methanol from combined reforming.

Both dimethyl carbonate processes are not as profitable as the production costs are equal to the selling price of the product and by-product (average selling price of 1230 USD per ton). Again, the process via methanol from combined reforming is not negative $NetCO_2$, however, it is still lower than the $NetCO_2$ of the industrial

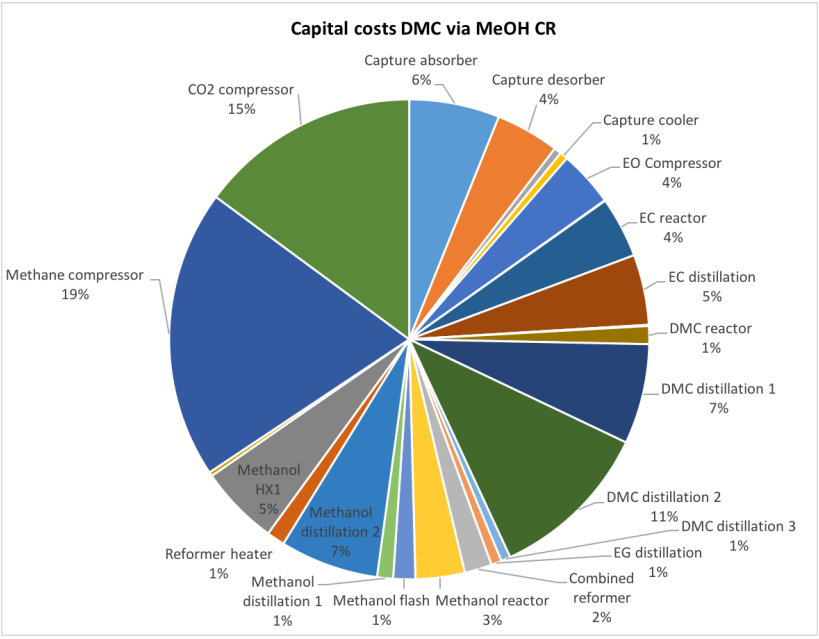

Figure 4.15. The breakdown of the purchase costs for the production of dimethyl carbonate via ethylene carbonate and methanol from combined reforming.

process (1.28 kg_{CO_2}/kg_{Prod}). The dimethyl carbonate process via methanol from direct hydrogenation is NetCO_2 negative, but, again, not as profitable.

The processes are also analyzed for hot spots. In the economic analysis and environmental analysis, the utility consumption of the individual units show that the methanol distillation and the dimethyl carbonate downstream processes are hot spots that should be targeted for further improvement to make the processes more sustainable (economically and environmentally).

4.3 Stage 3: Innovation

The processes from Stage 2 have hot spots in the high utility consumption for the methanol distillation (for both dimethyl ether and dimethyl carbonate processes) and energy demand in the dimethyl carbonate downstream separation processes. In Stage 3, the goal is to address these hot spots, by applying process intensification and hybrid methods, as process integration has already been considered in the base case design.

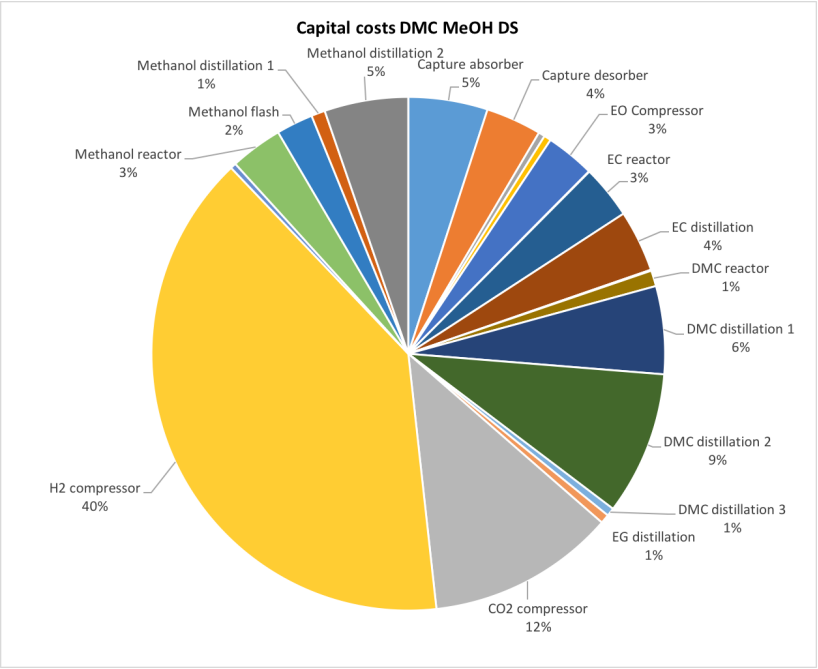

Figure 4.16. The breakdown of the purchase costs for the production of dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation.

4.3.1 Hybrid method

The hybrid method for distillation-membrane sequences is suited for the application to systems where distillation is energy intensive, and is therefore applied to the methanol distillation. In the methanol part of the carbon dioxide capture and conversion process, the distillation sequence needs to achieve high purity methanol. As a result, the column is large and has a high duty in the reboiler and the condenser. This can be addressed by applying the method of Tula et al. (2017) for hybrid distillation-membrane sequences. First, the driving force diagram is generated and then the data from the database is extracted to obtain the energy for distillation to 90 mol% (the intermediate) and 99.5 mol% (the target). This difference is used to calculate the potential energy savings (a 42% potential savings) in the third step. Then, the hybrid methanol process is simulated for detailed stream and equipment information. The distillation column is re-designed to account for the reduced product purity, reducing the height from 30 meters to 12 meters and the duties by 35%. Finally, the membrane area and cost are calculated using the selectivity and permeability for the appropriate Pervatech membrane (800 square meters and a purchase cost of 3.3 million USD over the project time of 10 years). By applying

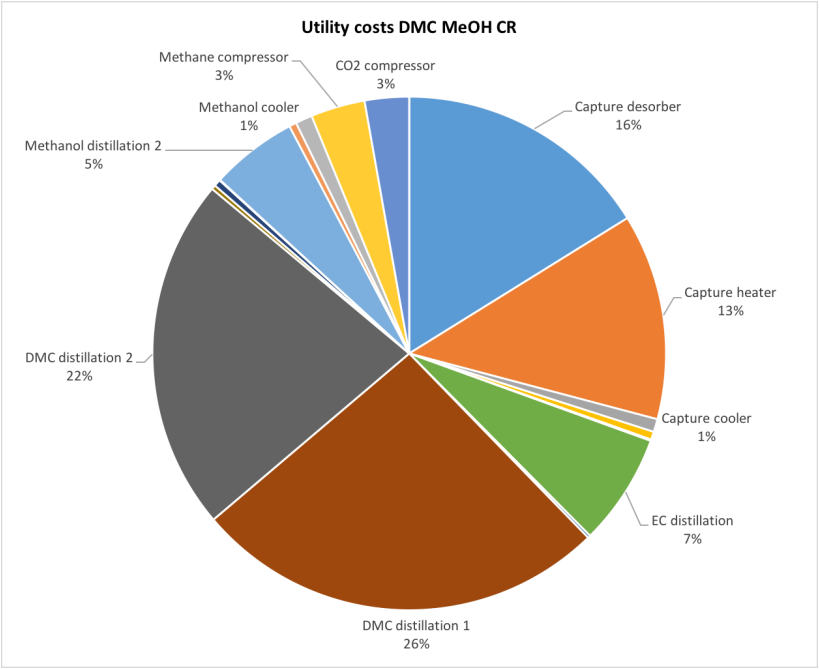

Figure 4.17. The breakdown of the utility costs for the production of dimethyl carbonate via ethylene carbonate and methanol from combined reforming.

this method, the single distillation column is replaced by a distillation column and a membrane, where the distillation column only purifies the product to 90 mol% and the membrane is used to achieve the target 99.5 mol%, resulting in the improved methanol processes shown in Figure 4.19. The simulation flowsheet and stream tables are provided in Appendix E.1.

The overall methanol processes are then designed and analyzed with the improved distillation design. As a result of the hybrid design, the capital cost of the entire methanol processes is increased by 4.6 million USD (over the 10 year span). This is a 2.2% increase for the combined reforming process and a 1.8% increase for the direct hydrogenation process. While the capital cost of the distillation column is reduced, the added membrane unit increases the capital costs. However, the operating costs are reduced by 22 million USD per year, which corresponds to a 11% reduction for combined reforming and a 9.4% reduction for direct hydrogenation. This large reduction in the operating costs, due to the reduced utility costs, results in a reduction of the NetCO_2 by 0.02 kg_{CO_2}/kg_{Prod}.

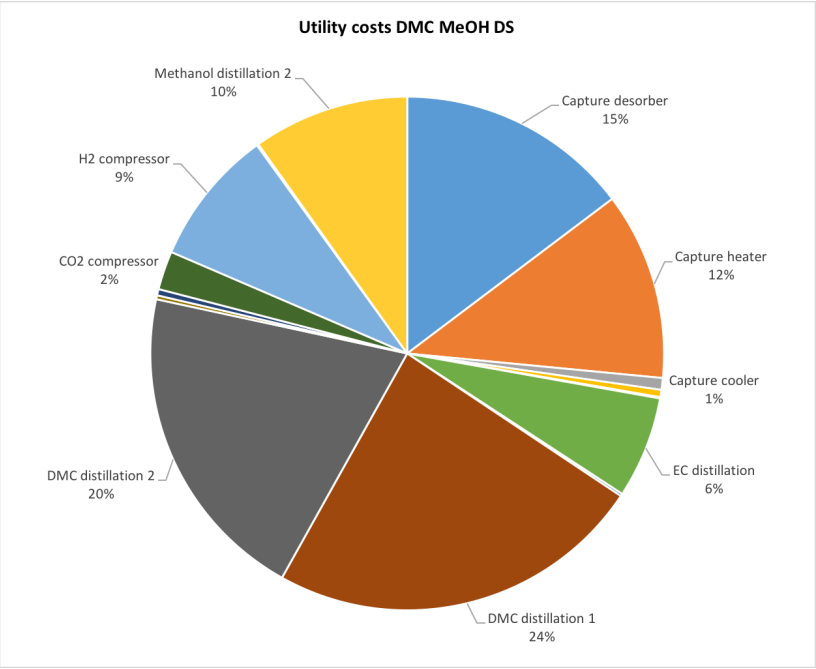

Figure 4.18. The breakdown of the utility costs for the production of dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation.

4.3.2 Process intensification

The dimethyl carbonate process is also very energy intensive. As a result of the azeotropes that form, the conventional separation involves numerous distillation columns to obtain the product at the desired purity. The goal of this stage is to reduce the utility consumption of the downstream processing. In order to address this, the phenomena-based method of process intensification is applied. In the first step of this method, the objective for Stage 3 (the reduction of the utility consumption of the dimethyl carbonate downstream processes) is stated as the objective for the intensification. Then, the flowsheet and simulation of the dimethyl carbonate production part of the processes from Stage 2 are used to obtain the mass and energy balances. The unit operations from the base case design are transformed to tasks and then phenomena. In the third step, the appropriate 15 phenomena building blocks (PBBs) are identified. Subsequently, these are combined to form simultaneous phenomena building blocks (SPBs), which are over 70 SPBs, after the use of connectivity rules (Kongpanna et al., 2016). Then, the alternatives are generated and compared by calculating the objective function, in this case profit (Profit = Sales - Material Costs - Utility Costs - Capital Costs). From this, it is de-

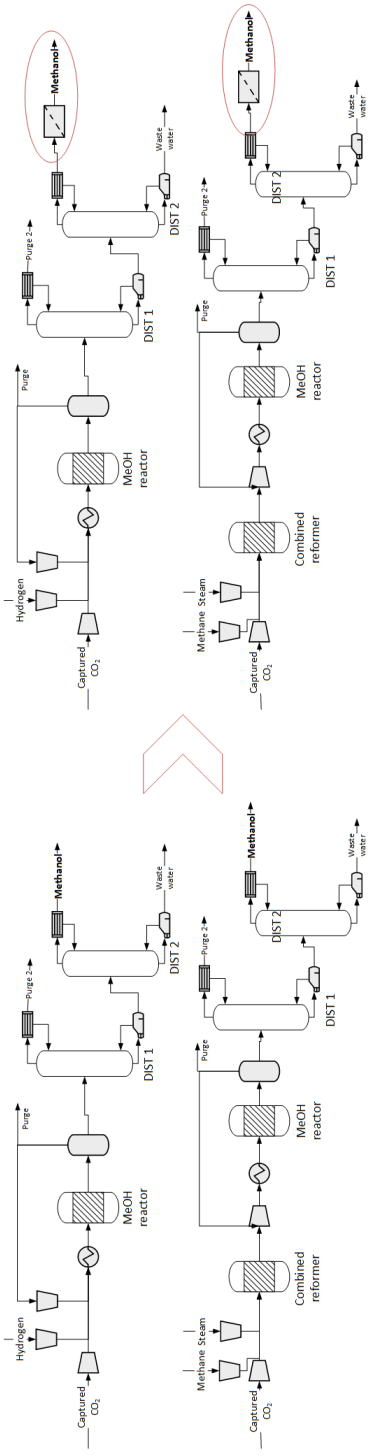

Figure 4.19. Process flow diagram of the methanol synthesis part of the carbon dioxide capture and conversion processes, and the hybrid design that is used to address the targets for improvement. The left is the direct hydrogenation and the right is the combined reforming process.

termined that dimethyl carbonate synthesis using reactive distillation, which allows for simultaneous reaction and separation, will provide the most improvement and the flowsheet is shown in Figure 4.20. The simulation flowsheet and stream tables are provided in Appendix E.2.

In this new design, the reactive distillation column is designed at 1 bar and has the reactive section in the bottom 26 stages and the separation part in the top 7 stages. With this setup, the ethylene carbonate can be nearly 100% converted and high purity ethylene glycol near the boiling point can be removed from the bottom of the column. The top of the column is methanol and dimethyl carbonate near the azeotrope. This can be separated as before with an increase in pressure. This design is simulated providing the detailed stream and equipment information. Due to the reduced amount of equipment and a reduction in the duty of the columns, this intensified design provides a reduction in capital cost, operating cost and NetCO_2. The capital cost is reduced by 15.9 million USD, which is 23% of the capital cost in the process. The operating cost is reduced by 7.8 million USD per year, which corresponds to 9% of the operating costs. Finally, the NetCO_2 is reduced by 0.01 kg_{CO_2}/kg_{Prod}. This improved and intensified process, when included in the integrated carbon dioxide capture and conversion processes yields the improved results listed in Table 4.10.

4.3.3 Overview of improved DME and DMC processes

For the capture and conversion of carbon dioxide to dimethyl ether, the target from Stage 2 was the reduction of the utility consumption in the methanol distillation column. This is achieved by replacing the methanol distillation with a distillation-membrane hybrid process, as described in Section 4.3.1. The rest of the process remains the same. With this new design (methanol with the hybrid distillation-membrane process), the economical and environmental analysis results in the values in Table 4.10.

The dimethyl carbonate processes targeted the utility consumption in the methanol distillation and the downstream dimethyl carbonate processing. The processes are improved by implementing the hybrid methanol distillation-membrane process described in Section 4.3.1 and the reactive distillation intensified dimethyl carbonate process as explained is Section 4.3.2. As a result of the combined improvements to the methanol distillation and dimethyl carbonate downstream processing, the analysis values yield a reduction in the capital costs, operating costs and NetCO_2 for the integrated carbon dioxide capture and conversion process. The important analysis results for the two dimethyl carbonate routes are also listed in Table 4.10.

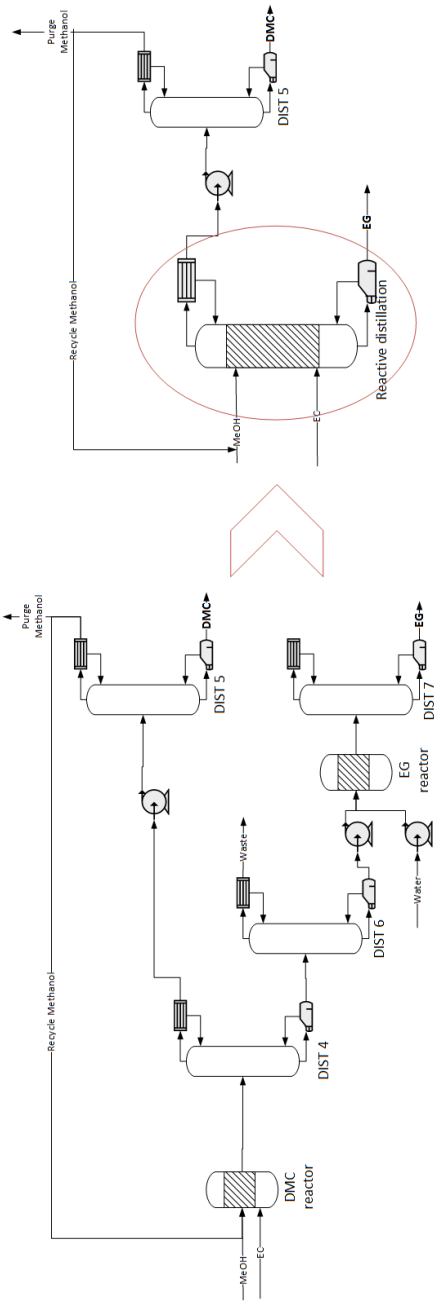

Figure 4.20. Process flow diagram of the dimethyl carbonate (DMC) synthesis part of the carbon dioxide capture and conversion processes, and the intensified design (using reactive distillation) that is used to address the targets for improvement.

Table 4.10. The overall results of the improved dimethyl ether and dimethyl carbonate processes. For dimethyl ether, the methanol processes have been improved via a hybrid distillation-membrane sequence. For dimethyl carbonate, the methanol processes have also been improved via the hybrid distillation-membrane sequence and the intensified dimethyl carbonate synthesis part with reactive distillation.

	improved DME with CR MeOH	**improved DME with direct MeOH**	**improved DMC via EC with CR MeOH**	**improved DMC via EC with direct MeOH**
Integrated process				
CAPEX (MM USD)	264.4	312.5	349.1	397.2
OPEX (MM USD/y)	263.6	291.8	349.6	377.8
NetCO_2 ($kg_{CO_{2,eq}}/kg_{Prod}$)	0.06	-0.19	0.01	-0.25
Production cost (USD/t)	710	827	1014	1053
Global CO_2 reduction (MM $t_{CO_{2,eq}}$/y)	-10.3	-40	-1.27	-1.53

4.3.4 Other innovative processes

In addition to the hybrid and intensified processes for the dimethyl ether and dimethyl carbonate processes presented here, Stage 3 has been applied to some other processes, including integration of methanol (Roh et al., 2016b) and intensification of dimethyl carbonate via other routes(such as via propylene carbonate and urea) (Babi et al., 2015; Kongpanna et al., 2015, 2016). For dimethyl carbonate via propylene carbonate and urea, the use of reactive distillation, pervaporation and membrane reactors result in more sustainable, intensified processes. All simulations that are available are listed in the simulation library, which can be found in Appendix B.3 Table B.3.

4.3.5 Discussion Stage 3 results

Stage 3 applies the methods for hybrid distillation-membrane design and phenomena-based process intensification to address the targets for improvement, which are the reduction of utilities in the methanol distillation and the dimethyl carbonate downstream separation. The application of these two methods results in more sustainable processes with reduced production costs and a reduced NetCO_2.

The production costs of dimethyl ether are reduced by 70 USD per ton. Despite

the small increase in capital costs, the large decrease in utility costs results in an overall reduction. The capital cost of the integrated processes have a capital cost increase of 1.9% and 1.6%, for dimethyl ether via methanol from combined reforming and dimethyl ether via methanol from direct hydrogenation, respectively. The operating costs are decreased by 7.7% and 7.0%, respectively. In addition, the $NetCO_2$ is decreased by 0.02 $kg_{CO_{2,eq}}/kg_{Prod}$ for both methanol synthesis routes. However, while the process via combined reforming is still positive $NetCO_2$, it is less than the industrial process.

The improved dimethyl carbonate processes have reduced capital costs, operating costs and $NetCO_2$. The decrease in the capital cost of the intensified dimethyl carbonate process is able to offset the increase in capital cost of the hybrid methanol distillation-membrane process. The overall reduction in capital costs for the processes is 3.5% and 3.0% for the dimethyl carbonate production via ethylene carbonate and methanol from combined reforming and dimethyl carbonate production via ethylene carbonate and methanol from direct hydrogenation, respectively. The utility costs are reduced 5.8% and 5.5%, respectively. This corresponds to a 125 USD per ton reduction in the production cost. The overall $NetCO_2$ is reduced by 0.03 $kg_{CO_{2,eq}}/kg_{Prod}$. Again, the process via combined reforming is still positive $NetCO_2$.

While both dimethyl ether and dimethyl carbonate can be made via carbon dioxide conversion routes that are sustainable with the framework, the production cost is still high and therefore the profit margin is small. Through the incorporation of the hybrid distillation-membrane process and reactive distillation (intensified) process, the base case design can be made more sustainable and the targets for improvement are addressed. The processes using methanol from direct hydrogenation are able to reduce more carbon dioxide. However, the cost of the hydrogen needed, is currently too high when compared with the methanol from combined reforming syngas. In order to make these carbon dioxide capture and conversion processes more economically competitive, hydrogen needs to be cheaper and more sustainable and the carbon dioxide capture processes need to be given incentives to offset the capture cost.

4.4 Summary of results and discussion

The developed framework has been applied to the design of carbon dioxide capture and converison processes to value-added chemicals. By considering seven scenarios in Stage 1, it is possible to evaluate the influence that different parameters have on the optimization. Then, four processes to dimethyl ether and dimethyl carbonate

are designed and analyzed in Stage 2. These processes are profitable and carbon dioxide reducing. However, the profit is low as the production costs are close to the selling prices. The energy consumption and cost of the methanol distillation and dimethyl carbonate production can be improved and the targets for improvement are determined to be to reduce the energy consumption of the methanol distillation and the dimethyl carbonate downstream separation. In Stage 3, through the use of a hybrid distillation-membrane in the methanol distillation and an intensified reactive distillation process for the dimethyl carbonate, the targets can be addressed. Overall, the operating costs and $NetCO_2$ of the processes are reduced by this. Through the application of the computer-aided framework, more sustainable design alternatives for the production of dimethyl ether and dimethyl carbonate are obtained.

The results show that there is a trade-off in the profitability and the carbon dioxide reduction for most processes. In addition, while most processes are carbon dioxide reducing (they emit less carbon dioxide than the industrial standard process), it is difficult to make the processes $NetCO_2$ negative. This is the result of the need for sustainable hydrogen and energy for these processes. In addition, the overall impact of carbon dioxide capture and utilization processes is minimal as only a fraction of the emissions can be reduced.

Chapter 5

Perspectives

Summary and significance:

In this chapter, some perspectives on carbon dioxide capture and utilization are presented. Through the development and implementation of the framework, insights are obtained on the potential and some of the limitations of carbon dioxide capture and utilization processes. These include the interaction it can play with existing technology and new technology, the need for other sustainable materials, in particular hydrogen and energy, and the role that CCU can play in addressing climate change and mitigating emissions.

Outline:

Sustainable carbon dioxide capture and utilization, particularly conversion, processes can be designed according to the presented framework (see Chapter 3), as is shown through the application (see Chapter 4). However, in the application, it becomes evident that there is often a trade-off in the profitability and the carbon dioxide that can be reduced. In addition, the type of the energy supply and other raw materials influence the ability of the process to reduce carbon dioxide as well as the profitability. In the next three sections, the need for sustainable raw materials and energy, the interaction with existing industrial processes, and the potential role of carbon dioxide capture and utilization processes can have are investigated.

5.1 Need for sustainable hydrogen and energy

Carbon dioxide capture and utilization, particularly conversion, often requires electricity and hydrogen. The processes use energy in compression and separation. In addition, the processes require certain reactants that carry the energy needed to react with the stable carbon dioxide molecule. Hydrogen is a common reactant that achieves this. However, the energy and the hydrogen that are used need to be sustainable in order for the entire carbon dioxide capture and conversion process to be sustainable.

Sustainable energy can be produced from renewable or alternative sources, including wind, water, solar, biomass and waste. However, these technologies are still being further developed to be competitive and efficient. Currently, therefore, these energy sources are still being expanded and are not able to supply the needed amounts. In order to achieve the goals of carbon mitigation, the development of these new energy sources and technologies is needed.

Traditionally, hydrogen is produced via steam methane reforming (SMR) of natural gas or coal gasification (Häussinger et al., 2011). However, these two processes result in a large amount of carbon dioxide emissions, which is not sustainable, especially for processes with the goal of reducing carbon dioxide emissions. For carbon dioxide capture and conversion processes, using hydrogen that is not sustainable results in higher emissions than can be utilized. Therefore, alternatives need to be evaluated for obtaining the hydrogen necessary for the conversion process; the hydrogen can be obtained via more sustainable means or from waste streams in industrial processes. Around the globe there are waste streams containing hydrogen that are generated in industrial plants, such as refineries or ammonia plants (Häussinger et al., 2011). The quantity and composition of these streams varies. However, most industries currently reuse these waste streams as fuel. These waste streams can be considered free, except for the associated replacement of

the heating value in the processes. In spite of the presence of some impurities, the utilization of such waste streams may become a favorable option. The exact amount of these streams and the cost of replacing them is currently not well publicized, and therefore other options for sustainable hydrogen are also needed. Alternatively, hydrogen can be produced via electrolysis of water using renewable sources of energy, such as water, solar, wind or biomass, to power the electrolysis. Using these energy sources results in hydrogen that emits less carbon dioxide than the traditional routes (SMR or gasification) (Carbon Recycling International (CRI), 2017). The influence of the hydrogen source on the $NetCO_2$ and cost of production for methanol is investigated by Roh et al. (2016b). As these results show, for all the cases considered, it is evident that less $NetCO_2$ emissions are obtained compared to hydrogen from steam methane reforming. Nevertheless, the methanol production costs for all the renewable hydrogen feed source cases exceed the methanol market price.

While sustainable energy and hydrogen is needed to ensure that the carbon dioxide capture and conversion processes are $NetCO_2$ reducing, further development or financial compensation are needed to improve the economics of the processes. Currently, the sustainable hydrogen and energy are too expensive and make the processes using carbon dioxide less competitive.

5.2 Interaction with other technology and existing infrastructure

In addition to the sustainability of the raw materials and energy, the realistic implementation of carbon dioxide capture and conversion needs to be considered.

The first element that needs to be discussed is the compatibility with existing infrastructure. While all the reduction methods need to be considered, the promise of carbon capture and utilization technology lies not only in the economic potential, but also in the similarity to existing technology. While some of the catalysts and solvents still are being developed, the general technology already exists (pumps, columns, tanks, etc.). Therefore, this can be quickly implemented in industrial settings. In addition, it is compatible with pipelines and other transportation infrastructure. The products formed in the utilization processes are traditional products that have existing infrastructure for the supply chain. In contrast, sequestration technology and innovative energy reducing technology, still needs to be developed and therefore cannot be directly implemented in the current infrastructure, and technology with improved efficiency still needs to be developed.

There is potential in carbon dioxide capture and utilization in integration with

other new technology. Carbon dioxide emissions are a waste material that can be used as a feedstock. Similarly, certain biomass processes are being developed from material waste products. The goal of these processes is to use such feedstocks to develop more sustainable energy and products. However, while these processes use renewable and alternative feedstocks, they are not always more sustainable. Especially since they also produce emissions to some extent. Therefore, carbon dioxide capture and utilization processes can be integrated with such new and innovative processes to make use of the emissions and produce more of the same or other products. This is considered by the work of Martín and Grossmann (2016). Martín and Grossmann (2016) designed a carbon dioxide hydrogenation-based methanol production facility integrated with switchgrass gasification units that produce the syngas for methanol production. The carbon dioxide feedstock is captured from the syngas produced from the switchgrass gasification and the hydrogen feedstock is produced via water splitting with wind and solar power. They conclude that the designed process can only be used in regions where wind velocity and solar radiation are high enough such as the US Midwest or the South of Europe. Similarly, the interactions for other products and bioprocesses can be investigated. There is the potential that the bioprocesses have by-products that can be raw materials for carbon dioxide conversion processes and vice versa.

Carbon dioxide capture and utilization technology, as mentioned, is promising, however, the interaction with the other reduction methods is important. Carbon capture and sequestration is immature and the consequences are unknown. There is also no economic incentive (via carbon tariffs or tax breaks for capture) to capture and sequester as there is no valuable product produced and there are only costs. Alternatively, methods of improving the efficiency of processes can truly solve part of the problem of increasing emissions as they do not just transform or remove emissions after being produced, but rather the emissions are avoided. However, these technologies have not been developed yet. Also, there is a cost associated with developing and replacing the equipment with more efficient technology. Meanwhile, carbon dioxide capture and utilization, at least in part, can be directly integrated in industry and power plants as the equipment and products are the same. Thereby, it can serve as an immediate and intermediate step in the solution towards reducing carbon dioxide emissions. In addition, the revenue from the commercial products can be used to offset the costs of developing and implementing the other reduction methods. In this way, carbon capture and utilization is especially promising an immediate solution and a bridge between current and future technology. As, the amount that can be reduced with utilization is limited (North and Styring, 2015), it is only part of the solution.

5.3 Role of CCU in carbon mitigation

The sustainable design of carbon dioxide capture and utilization processes can be realized. Through the application of the framework, this has been shown for the production of dimethyl ether and dimethyl carbonate. Both dimethyl ether and dimethyl carbonate can be produced via carbon dioxide conversion processes that are profitable and carbon dioxide reducing. However, it is difficult to make the processes $NetCO_2$ negative. Only the routes using direct hydrogenation with hydrogen from sustainable sources are $NetCO_2$ negative, in the application of the developed framework. The designed processes shown in Chapter 4, however, are often more expensive than the current industrial standard as a result of the expensive materials and energy required. In addition, the amount of carbon dioxide emissions that can be reduced is small compared to the global emissions. As is shown in Figure 5.1, the amount of emissions that can be reduced by producing various products from carbon dioxide capture and conversion is limited. Of the hundreds of power plants, only a fraction (approximately 1%) can be reduced in this way.

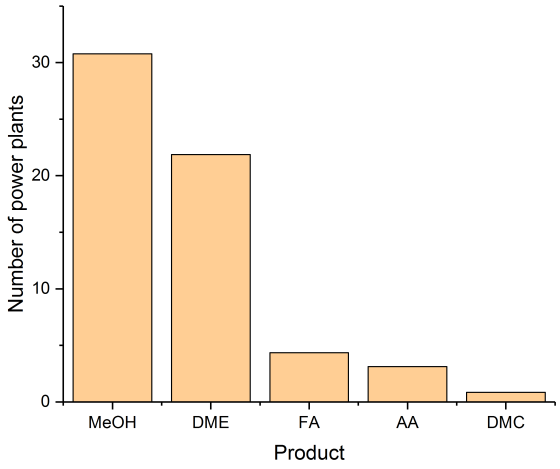

Figure 5.1. The number of power plants (considering emissions from a 150 MW coal-fired power plant) whose carbon dioxide emissions can be offset by the production of the products via carbon dioxide capture and conversion processes.

Although carbon dioxide capture and conversion processes are sustainable and reduce carbon dioxide, only a fraction can be reduced due to the limited number of products and the small demand. The largest impact comes from methanol and dimethyl ether, due to the highest demand. In order for carbon dioxide capture and

conversion to play a substantial role in reducing carbon dioxide emissions, more bulk chemicals produced via carbon dioxide conversion should be investigated.

Climate change cannot be ignored and methods of addressing this need to be considered. In order to ensure that the damage is not irreversible, drastic and immediate actions are needed. Alone, carbon dioxide capture and utilization can only offset a fraction of the emissions. However, it can serve as a bridge between existing technology and future practices. In order to realize its implementation, along with the research and development for future technology, both economic and regulatory incentives are required. The costs of changing the existing processes and the production costs of the utilization processes is too high to motivate in the current situation. Carbon dioxide tariffs and incentives for innovative technology are necessary to motivate commercial and industrial realization. Sustainability and the reduction of carbon dioxide emissions requires the attention of research and development to provide technical solutions, regulatory incentives to motivate the economic shift to alternative processes, and societal acceptance of these alternative technologies.

Chapter 6

Conclusions & Future work

6.1 Conclusions

In order to help address climate change issues and reduce carbon dioxide emissions, a framework for the sustainable design of carbon dioxide capture and utilization processes, particularly conversion processes, has been developed and applied. This computer-aided framework consists of three stages: (1) synthesis, (2) design, and (3) innovation. By decomposing the problem into these three stages, simpler models are used to first select from a large number of process alternatives and then more detailed models are used to rigorously design, analyze and improve the optimal process(es).

The framework has been used to design sustainable carbon dioxide capture and conversion processes from coal-fired power plant flue gas to value-added chemicals. The goal is to determine the optimal processing route to produce a product and subsequently design the process to be sustainable. This considers the single feedstock and the capture of carbon dioxide using monoethyl amine (MEA) absorption. In Stage 1, the superstructure-based optimization method is used to determine the optimal route(s) from a large number of alternatives. Seven different scenarios, which vary elements of the objective function or parameters, are considered to evaluate the influence of key model parameters (prices, reaction conversion, etc.) on the optimization. The results show that the primary influence on the selection of the optimal route is the product and material costs. In addition, when the demand for the products is considered, it becomes evident that there is often a trade-off in the profit and the carbon dioxide reduction. By considering the processes with the largest impact in carbon dioxide emission reduction and the profitability, four processes, producing dimethyl ether or dimethyl carbonate from carbon dioxide, are selected. These four routes are:

1. Dimethyl ether synthesis via methanol from combined reforming syngas

2. Dimethyl ether synthesis via methanol from direct hydrogenation of carbon dioxide

3. Dimethyl carbonate synthesis via ethylene carbonate and methanol from combined reforming syngas

4. Dimethyl carbonate synthesis via ethylene carbonate and methanol from direct hydrogenation of carbon dioxide.

After the design and analysis in Stage 2, all four processes can be profitable and carbon dioxide reducing. However, economic evaluation has shown small profit, as the production costs are close to the selling price. Also, only the routes using methanol from direct hydrogenation are NetCO_2 negative, where more carbon dioxide is utilized than emitted. In addition, the breakdown of the utility costs and purchase costs for the four processes indicate that the methanol distillation (for all four processes) and dimethyl carbonate downstream process (for the two dimethyl carbonate processes) are hot spots and can be improved (targets for improvement). In Stage 3, by applying the methods for design of hybrid distillation-membrane separations and phenomena-based intensification, more sustainable processes are found to address these targets. The methanol distillation is improved by introducing a hybrid distillation-membrane process, reducing the utility consumption by approximately 10%. The dimethyl carbonate process is intensified by introducing reactive distillation, thereby reducing the number of separation steps required. The intensified process reduces the capital costs and the operating costs by 23% and 9%, respectively.

The computer-aided framework requires large amounts of data, which motivates the development of databases to store the information. This includes the reaction path synthesis database and the superstructure database. The reaction path synthesis database stores all the information collected from the application of the reaction path synthesis method, which is incorporated in the framework. These reactions are stored so they may motivate further research in certain conversion reactions, as not all have kinetic information available now. The superstructure database is systematically structured and contains a collection of carbon dioxide capture and conversion technologies, which previously was not organized. This organizes information pertaining to the process technologies, including reactions, separations, and utilities. This database can facilitate the storage of alternatives for comparison among alternatives with future technologies in Stage 1.

The application of the framework and the scenarios considered also provide some insights into: (1) the role of carbon dioxide capture and utilization in carbon mitigation, (2) the importance of sustainable hydrogen and energy, and (3) the integration of these processes with infrastructure, industry and other reduction methods. While carbon dioxide capture and utilization processes can reduce carbon dioxide emissions, they can only offset a fraction of the emissions. Therefore, it is necessary that other carbon dioxide reduction methods are considered in conjunction. As carbon dioxide capture and utilization processes are technologically mature, they can serve as a bridge between the existing status of industry and future technologies. They are able to provide an economic incentive that can help offset the costs of capture and the development and implementation of new, more efficient technology. However, in order to make these processes competitive, the development of cheaper, more sustainable hydrogen and energy will play a large role. Without the production of energy and hydrogen from renewable and alternative sources, such as wind, solar, biomass and waste, the development of sustainable processes cannot address the global issues.

In order to address climate change issues, a variety of drastic measures are needed. Carbon dioxide capture and utilization can play an integral part in the transition from current practices to future, more sustainable practices. This project introduces a framework that can help in the sustainable design of these carbon dioxide capture and utilization processes. In addition, some insights on the sustainability and role of carbon dioxide capture and utilization processes are presented.

6.2 Future work

While a framework for the sustainable design of carbon dioxide capture and utilization processes has been developed and applied, there are still areas for future work.

First of all, the developed framework has only been applied considering one carbon dioxide emission source and one method of capture. However, it would greatly expand this work, if multiple carbon dioxide sources and capture methods were considered. This would not only provide insight into what conversion process and product to produce, but what capture process to use for the carbon dioxide source.

Secondly, the application of the framework is only considered for single locations. That is, the capture and conversion processes are located together. However, this will not always be the case. Therefore, the transportation between capture and conversion locations needs to be considered. Depending on the location of the

emission source, the chemical conversion process cannot be easily incorporated into the infrastructure. The chemical industry has already established a market for the products that would be produced and has the equipment and necessary materials for the conversion processes. In addition, the locations considered vary the utility and chemical prices. However, when these are considered, the varying cost of the capture process is not considered, as this part of the process is fixed. Therefore, different locations and the transportation between them should be considered to assess the economic feasibility and the environmental impact with transportation. Additionally, the impact of the corresponding utility price on the selection of the optimal capture process and cost can be investigated.

The databases that are incorporated in the framework should also be expanded. The superstructure database provides an organized collection of the conversion technologies that have been developed to different value-added products. This database should be expanded as more process technologies are developed (including new catalysts and reactors) and with more feedstock and capture alternatives. This organized database provides a source that can be used for further research in carbon dioxide capture and conversion processes. Reaction path synthesis is also applied to determine all the reactions converting carbon dioxide. While there are numerous literature sources, this systematic method allows the systematic generation of all reactions also those that have not been investigated experimentally. The result of this can help guide research on which reactions should be focused on as they have potential for carbon dioxide conversion.

As carbon dioxide capture and utilization is a field of growing importance, the continuation and elaboration of this work can help in the sustainable design of the processes and in indicating the need for other carbon dioxide reduction methods.

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Appendix A

Dissemination of the PhD results

This PhD thesis represents the culmination of a three-year PhD study at the Technical University of Denmark. As part of this work, the PhD project and the results obtained have been disseminated via journal publications and conference presentations and proceedings. Some of the publications published are also reflected in parts of this thesis. The following publications, in chronological order, reflect results from this thesis:

1. R. Frauzem, P. Kongpanna, K. Roh, J. H. Lee, V. Pavarajarn, S. Assabumrungrat, and R. Gani. Sustainable process design: Sustainable process networks for carbon dioxide conversion. In F. You, editor, *Sustainability of Products, Processes and Supply Chains*, volume 36, pages 175–195. Elsevier BV, 2015

2. K. Roh, R. Frauzem, T. B. Nguyen, R. Gani, and J. H. Lee. A methodology for the sustainable design and implementation strategy of CO_2 utilization processes. *Comput. Chem. Eng.*, 91:407–421, aug 2016b

3. M.-O. Bertran, R. Frauzem, L. Zhang, and R. Gani. A generic methodology for superstructure optimization of different processing networks. In Z. Kravanja, editor, *Proceedings of the 26th European Symposium on Computer Aided Process Engineering – ESCAPE 26*, pages 685–690, Portorož, Slovenia, 2016. Elsevier BV

4. K. Roh, R. Frauzem, R. Gani, and J. H. Lee. Process systems engineering issues and applications towards reducing carbon dioxide emissions through conversion technologies. *Chem. Eng. Res. Des.*, 116:27–47, dec 2016a

5. M.-O. Bertran, R. Frauzem, A.-S. Sanchez-Arcilla, L. Zhang, J. M. Woodley, and R. Gani. A generic methodology for processing route synthesis and design

based on superstructure optimization. *Comput. Chem. Eng.*, 106(ESCAPE26 Special Issue):892 – 910, 2017

6. R. Frauzem, J. M. Woodley, and R. Gani. Application of a computer-aided framework for the design of CO_2 capture and utilization processes. In A. Espuña, M. Graells, and L. Puigjaner, editors, *Proceedings of the 27th European Symposium on Computer Aided Process Engineering – ESCAPE 27*, volume 40 of *Comput. Chem. Eng.*, pages 2653–2658. Elsevier BV, 2017

In addition, the results were presented at the following conferences, also in chronological order:

1. American Institute of Chemical Engineers (AIChE) Annual Meeting 2014 in Atlanta, Georgia, USA: oral presentation titled "Sustainable Process Networks for CO_2 Conversion"

2. 4th International Congress on Sustainability in Science and Engineering (ICOSSE) 2015 in Balatonfüred, Hungary: oral presentation titled "Synthesis and Design of a Sustainable CO_2 Utilization Network"

3. Process Systems Engineering (PSE) 2015 and the 25th European Symposium on Computer Aided Process Engineering (ESCAPE25) in Copenhagen, Denmark: poster presentation titled "Formulation of a Network and the Study of Reaction Paths for the Sustainable Reduction of CO_2 Emissions"

4. 2015 CAPEC-PROCESS Annual Meeting in Copenhagen, Denmark: poster presentation titled "Formulation of a Network and the Study of Reaction Paths for the Sustainable Reduction of CO_2 Emissions"

5. 10th European Congress of Chemical Engineering (ECCE) in Nice, France: poster presentation titled "Formulation and Design of a CO_2 Utilization Network Detailed Through a Conceptual Example"

6. American Institute of Chemical Engineers (AIChE) Annual Meeting 2015 in Salt Lake City, Utah, USA: oral presentation titled "A Methodology for a Sustainable CO_2 Capture and Utilization Network"

7. American Institute of Chemical Engineers (AIChE) Annual Meeting 2015 in Salt Lake City, Utah, USA: oral presentation titled "A Method for Sustainable Carbon Dioxide Utilization Process Synthesis and Design"

8. 26th European Symposium on Computer Aided Process Engineering (ESCAPE26) in Portorož, Slovenia: oral presentation titled "A generic methodology for

superstructure optimization of different processing networks" presented by colleague Maria-Ona Bertran

9. 14th International Conference on Carbon Dioxide Utilisation 2016 in Sheffield, UK: oral presentation titled "A generic methodology for the design of sustainable carbon dioxide utilization processes using superstructure optimization"

10. 2016 KT Consortium Annual Meeting in Kongens Lyngby, Denmark: oral presentation titled "Sustainable design of carbon dioxide capture and utilization processes"

11. American Institute of Chemical Engineers (AIChE) Annual Meeting 2016 in San Francisco, California, USA: oral presentation titled "Systematic framework for carbon dioxide capture and utilization processes to reduce the global carbon dioxide emissions"

12. American Institute of Chemical Engineers (AIChE) Annual Meeting 2016 in San Francisco, California, USA: oral presentation titled "Application of a systematic methodology for sustainable carbon dioxide utilization process design"

13. 2017 KT Consortium Annual Meeting in Elsinor, Denmark: oral presentation titled "Sustainable CO_2 Capture & Conversion Technologies"

14. 27th European Symposium on Computer Aided Process Engineering (ESCAPE27) in Barcelona, Spain: oral presentation titled "Application of a computer-aided framework for the design of CO_2 capture and utilization processes"

15. American Institute of Chemical Engineers (AIChE) Annual Meeting 2017 in Minneapolis, Minnesota, USA: oral presentation titled "The Design of Sustainable Carbon Dioxide Capture and Conversion Processes Considering Various Locations, Products and Routes"

Finally, parts the PhD project have also been done in collaboration with Master's students and visiting international students. This collaboration is reflected in the following publications and presentations:

1. K. Fjellerup. Sustainable process networks for carbon dioxide conversion. mathesis, Technical University of Denmark, 2015

2. B. H. T. Nguyen. Techno-economic evaluation of CO_2 utilization processes: Hydrogenation, bi- and tri-reforming of CO_2 into methanol production. mathesis, Chulalongkorn University, 2015

3. C. C. Plaza. Sustainable carbon dioxide capture and conversion process design. mathesis, Technical University of Denmark, June 2016

4. W. Prasertsri, R. Frauzem, U. Suriyapraphadilok, and R. Gani. Sustainable DME synthesis-design with CO_2 utilization. In Z. Kravanja and M. Bogataj, editors, *26th European Symposium on Computer Aided Process Engineering*, pages 1081–1086, Portorož, Slovenia, 2016. Elsevier BV

5. 26th European Symposium on Computer Aided Process Engineering (ESCAPE26) in Portorož, Slovenia: oral presentation titled "Sustainable DME synthesis-design with CO_2 utilization" presented by Weeranut Prasertsri

6. A. Wisutwattana, R. Frauzem, U. Suriyapraphadilok, and R. Gani. Intensification of ethylene glycol production process. In A. Espuña, M. Graells, and L. Puigjaner, editors, *Proceedings of the 27th European Symposium on Computer Aided Process Engineering – ESCAPE 27*, volume 40 of *Comput. Chem. Eng.*, pages 1135–1140. Elsevier BV, 2017

7. 27th European Symposium on Computer Aided Process Engineering (ESCAPE27) in Barcelona, Spain: poster presentation titled "Intensification of ethylene glycol production process" presented by Apiwit Wisutwattana

Through these papers and presentations and any future papers and presentation, this PhD project has been presented internationally.

Appendix B

Superstructure

Stage 1 of the framework involves the superstructure-based optimization; the superstructure model, the databases and the other tools of this stage are presented in Section 3.2. For the databases presented, further information about the information contained in them is presented in Section B.1, B.2 and B.3.

B.1 Superstructure database

The superstructure database is structured and contains the statistics presented in Section 3.2.2. The details on feedstocks, products, intervals, etc. are presented in this appendix.

Table B.1. Components in the database.

ComponentID	ComponentName	Formula	MolarWeight
carbondioxide	carbon dioxide	CO2	44
carbonmonoxide	carbon monoxide	CO	28
hydrogen	hydrogen	H2	2
water	water	H2O	18
methane	methane	CH4	16
methanol	methanol	CH4O	32
dimethylether	dimethyl ether	C2H6O	46
ammonia	ammonia	NH3	17
urea	urea	N2H4CO	60
propyleneoxide	propylene oxide	C3H6O	58
propylenecarbonate	propylene carbonate	C4H6O3	102
ethyleneoxide	ethylene oxide	C2H4O	44
ethylenecarbonate	ethylene carbonate	C3H4O3	88
dimethylcarbonate	dimethyl carbonate	C3H6O3	90
propyleneglycol	propylene glycol	C3H8O2	76
ethyleneglycol	ethylene glycol	C2H6O2	62
formicacid	formic acid	CH2O2	46
glucose	glucose	C6H12O6	180
succinicacid	succinic acid	C4H6O4	118
aceticacid	acetic acid	C2H4O2	60
methylacetate	methyl acetate	C3H6O2	74
ethane	ethane	C2H6	30
propane	propane	C3H8	44
nitrogen	nitrogen	N2	28
hydrogensulfide	hydrogen sulfide	H2S	34
butane	butane	C4H10	58
oxygen	oxygen	O2	32
argon	argon	Ar	40
monoethylamine	monoethylamine	C2H7N	45
ethylene	ethylene	C2H4	28
ethanol	ethanol	C2H6O	46
propanol	propanol	C3H8O2	60
monohydrogen	monohydrogen	H	1
malicacid	malic acid	C4H6O5	134
pyruvicacid	pyruvic acid	C3H4O3	88
butanol	butanol	C4H10O	74

Table B.2. Reaction sets in the database.

ReactionSetID	ReactionSetName	No. Reactions in Set	Sequential?
cr	combined reforming of natural gas to produce syngas (M=2)	1	no
dr	dry reforming of natural gas to produce syngas (M=1)	2	yes
meohdirsyn	MeOH synthesis from CO2 and H2	2	no
meohsyn	MeOH synthesis from syngas (M=2)	2	yes
meohsyn2	MeOH synthesis from syngas (M=1)	2	no
dmemeohsyn	DME synthesis from MeOH	1	no
dmedirsyn	DME synthesis from syngas (M=1)	3	yes
ureasyn	urea synthesis from NH3 and CO2	1	no
ecsyn	EC synthesis from EO and CO2	1	no
pcsyn	PC synthesis from PO and CO2	1	no
dmcdirsyn	DMC synthesis directly from CO2 and methanol	1	no
dmcureasyn	DMC synthesis from urea	1	no
dmcecsyn	DMC synthesis from EC	1	no
dmcpcsyn	DMC synthesis from PC	1	no
aasyn	acetic acid synthesis from methanol and CO	2	yes
fasyn	formic acid synthesis from CO2 and H2	1	no
etohsyn	ethanol synthesis from CO2 and H2	10	no
sasyn	succinic acid synthesis by glucose fermentation	4	no

Table B.3. Reactions in the database.

ReactionID	ReactionSetID	Components	Reaction
cr-1	cr	5	$3CH_4 + 2H_2O + CO_2 \leftrightarrow 4CO + 8H_2$
dr-1	dr	4	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$
dr-2	dr	4	$CO_2 + H_2 \leftrightarrow CO + H_2O$
meohdirsyn-1	meohdirsyn	4	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$
meohdirsyn-2	meohdirsyn	4	$CO_2 + H_2 \leftrightarrow CO + H_2O$
meohsyn-1	meohsyn	4	$CO + H_2O \leftrightarrow CO_2 + H_2$
meohsyn-2	meohsyn	4	$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$
meohsyn2-1	meohsyn2	3	$CO + 2H_2 \leftrightarrow CH_3OH$
meohsyn2-2	meohsyn2	4	$CO + H_2O \leftrightarrow CO_2 + H_2$
dmemeohsyn-1	dmemeohsyn	4	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$
dmedirsyn-1	dmedirsyn	4	$CO + H_2O \leftrightarrow CO_2 + H_2$
dmedirsyn-2	dmedirsyn	3	$CO + 2H_2 \leftrightarrow CH_3OH$
dmedirsyn-3	dmedirsyn	3	$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O$
ureasyn-1	ureasyn	4	$CO_2 + 2NH_3 \leftrightarrow NH_2CONH_2 + H_2O$
ecsyn-1	ecsyn	4	$CO_2 + C2H4O \leftrightarrow (CH_2O)_2CO$
pcsyn-1	pcsyn	4	$CO_2 + C_3H_6O \leftrightarrow CH_3(C_2H_3O_2)CO$
dmcdirsyn-1	dmcdirsyn	4	$CO_2 + 2CH_3OH \leftrightarrow OC(OCH_3)_2 + H_2O$
dmcureasyn-1	dmcureasyn	4	$NH_2CONH_2 + 2CH_3OH \leftrightarrow OC(OCH_3)_2 + 2NH_3$
dmcecsyn-1	dmcecsyn	4	$(CH_2O)_2CO + 2CH_3OH \leftrightarrow OC(OCH_3)_2 + (CH_2OH)_2$
dmcpcsyn-1	dmcpcsyn	4	$CH_3(C_2H_3O_2)CO + 2CH_3OH \leftrightarrow OC(OCH_3)_2 + C_3H_8O_2$
fasyn-1	fasyn	3	$CO_2 + H_2 \leftrightarrow CHOOH$
sasyn-1	sasyn	5	$C_6H_{12}O_6 + 2CO_2 + 4H \leftrightarrow 2C_4H_6O_4 + 2H_2O$
sasyn-2	sasyn	2	$C_6H_{12}O_6 + 2CO_2 \leftrightarrow 3CH_3COOH$
sasyn-3	sasyn	3	$C_6H_{12}O_6 \leftrightarrow 2CH_3COCOOH + 4H$
sasyn-4	sasyn	3	$C_6H_{12}O_6 + 2CO_2 \leftrightarrow COOHCH_2COHCOOH$
etohsyn-1	etohsyn	4	$2CO_2 + 6H_2 \leftrightarrow CH_3CH_2OH + 3H_2O$
etohsyn-2	etohsyn	4	$3CO_2 + 7H_2 \leftrightarrow CH_3COOCH_3 + 4H_2O$
etohsyn-3	etohsyn	4	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$
etohsyn-4	etohsyn	4	$2CO_2 + 7H_2 \leftrightarrow C_2H_6 + 4H_2O$
etohsyn-5	etohsyn	4	$4CO_2 + 13H_2 \leftrightarrow C_4H_10 + 8H_2O$
etohsyn-6	etohsyn	4	$3CO_2 + 10H_2 \leftrightarrow C_3H_8 + 6H_2O$

etohsyn-7	etohsyn	4	$3CO_2+9H_2 \leftrightarrow CH_3CH_2CH_2OH+4H_2O$
etohsyn-8	etohsyn	4	$CO_2+3H_2 \leftrightarrow CH_3OH+H_2O$
etohsyn-9	etohsyn	4	$4CO_2+12H_2 \leftrightarrow CH_3CH_2CH_2CH_2OH+7H_2O$
etohsyn-10	etohsyn	4	$CO_2+H_2 \leftrightarrow CO+H_2O$
aasyn-1	aasyn	4	$2CH_3OH+CO \leftrightarrow CH_3COOCH_3+H_2O$
aasyn-2	aasyn	4	$CH_3COOCH_3+H_2O \leftrightarrow CH_3COOH+CH_3OH$

Table B.4. Feedstocks in the database

FeedstockID	**FeedstockName**	**Components**	**LocationID**	**Price**
highpurCO2	high-purity CO_2	4	US	0 USD/t
MEACO2	CO_2 from MEA Capture	2	CA	74 USD/t
coalCO2_1	flue gas from coal-fired power plant	3	CA	0 USD/t
NG	natural gas for sweetening	12	US	37 USD/t

Table B.5. Utilities in the database.

UtilityID	**LocationID**	**Price**
electricity	US	0.0664 USD/kWh
hp steam	US	0.0066 USD/kg steam
coolingwater	US	0.00011 USD/kg CW

Table B.6. Products in the database

ProductID	LocationID	Price	Demand	Plant size
MeOH	US	0.48 USD/kg	70 million metric tons	0.75 million metric tons/year
H2O	US	0.00011 USD/kg		
DME	US	0.97 USD/kg	30 million metric tons	0.1 million metric tons/year
DMC	US	1 USD/kg	1 million metric tons	0.1 million metric tons/year
NH3	US	0.48 USD/kg	55 million metric tons	
EG	US	1.45 USD/kg	12 million metric tons	0.75 million metric tons/year
PG	US	2.06 USD/kg	1.5 million metric tons	0.1 million metric tons/year
EC	US	1.75 USD/kg	0.5 million metric tons	
AA	US	0.73 USD/kg	6 million metric tons	0.5 million metric tons/year
FA	US	0.74 USD/kg	0.75 million metric tons	0.1 million metric tons/year
SA	US	1.8 USD/kg	0.2 million metric tons	0.02 million metric tons/year
EtOH	US	1.13 USD/kg	75 million metric tons	0.3 million metric tons/year
CH4	US	0.37 USD/kg		

Table B.7. Materials in the database.

MaterialID	MaterialName	MaterialDescription
coalMEACO2	coalMEACO2	CO2 from MEA capture of coal-fired power plant flue gas
coalCO2_1	coalCO2_1	CO2-containing flue gas from coal-fired power plant
M1	coalCO2+MEA	coalCO2_1 mixed with MEA solvent
M2	loadedMEA	loaded MEA from CapABS1
M3	capturedCO2	CO2 captured from coal-fired power plant flue gas
M4	feedCR	feed mixture (CO2, CH4, H2O) for combined reforming
M5	feedDR	feed mixture (CO2, CH4) for dry reforming
M6	Crout	outlet of combined reforming reactor
M7	DR1out	outlet of dry reforming reaction 1
M8	DR2out	outlet of dry reforming reactor
M9	feedmeohdirsyn	feed mixture (CO2, H2) for methanol direct hydrogenation
M10	feedmeohsyn	feed mixture for methanol synthesis from syngas (M=2)
M11	feedmeohcosyn	feed mixture for methanol synthesis from syngas (M=1)
M12	feedfasyn	feed mixture (CO2, H2) for formic acid synthesis
M13	feedsasyn	feed mixture (CO2, glucose) for succinic acid synthesis
M14	feedetohsyn	feed mixture (CO2, H2) for ethanol synthesis
M15	meohdirsynout	outlet of methanol direct synthesis reactor
M16	meohsyn1out	outlet of methanol synthesis from syngas (M=2) reaction 1
M17	meohcosyn1out	outlet of methanol synthesis from syngas (M=1) with H2 addition
M18	meohcosyn2out	outlet of methanol synthesis from syngas (M=1) without H2 addition
M19	dmedirsyn1out	outlet of dme direct synthesis reaction 1
M20	fasynout	outlet of formic acid synthesis reactor
M21	sasynout	outlet of succinic acid synthesis reactor
M22	etohsynout	outlet of ethanol synthesis reactor
M23	meohsyn2out	outlet of methanol synthesis from syngas (M=2) reaction 2
M24	dmedirsyn2out	outlet of dme direct synthesis reaction 2
M25	dmedirsyn3out	outlet of dme direct synthesis reaction 3

M26	flash1.1out	raw methanol stream from flash 1.1
M27	flash1.2out	raw methanol stream from flash 1.2
M28	flash1.3out	raw methanol stream from flash 1.3
M29	dist1.1out	raw dme stream from dist 1.1
M30	flash1.4out	raw formic acid stream from flash 1.4
M31	reactex1.1	raw succinic acid from reactex 1.1
M32	flash1.5top	top product (raw methane) from flash 1.5
M33	flash1.5bottom	bottom product (raw ethanol) from flash 1.5
M34	flash1.6top	top product (raw CO) from flash 1.6
M35	flash1.6bottom	bottom product (raw methanol) from flash 1.6
M36	dist2.1out	raw methanol stream from dist 2.1
M37	dist2.2out	raw methanol stream from dist 2.2
M38	flash2.1out	raw methanol stream from flash 2.1
M40	dist2.4out	raw formic acid stream from dist 2.4
M41	vacdist2.1out	raw succinic acid from vacdist 2.1
M43	flash2.2out	raw methanol stream from flash2.2
M44	crystalizer3.1out	raw succinic acid stream from crystalizer 3.1
M45	dist3.5out	raw ethanol stream from dist 3.5
M46	dist3.6out	raw methanol stream from dist 3.6
M47	memb4.1out	CO stream from memb 4.1
M48	feedUreasyn	feed mixture (CO2, NH3) for urea synthesis
M49	feedECsyn	feed mixture (CO2, EO) for ethylene carbonate synthesis
M50	feedPCsyn	feed mixture (CO2, PO) for propylene carbonate synthesis
M51	ureasynout	oulet of urea synthesis
M52	ecsynout	outlet of ethylene carbonate synthesis
M53	pcsynout	outlet of propylene carbonate synthesis
M54	dist5.1out	raw urea stream from dist 5.1
M55	dist5.2out	raw ethylene carbonate stream from dist 5.2
M56	flash5.1out	raw propylene carbonate stream from flash 5.1
M57	feedDMCdirsyn	feed mixture (CO2, methanol) for DMC direct synthesis
M58	feedDMCureasyn	feed mixture(urea, methanol) for DMC synthesis from urea
M59	feedDMCECsyn	feed mixture (EC, methanol) for DMC synthesis from ethylene carbonate
M60	feedDMCPCsyn	feed mixture (PC, methanol) for DMC synthesis from propylene carbonate
M61	feedAAsyn	feed mixture (methanol, CO) for AA synthesis

M62	feedAA2syn	feed mxture (methanol, CO) for AA synthesis with membrane
M63	dmemeohsynout	outlet of dme synthesis from methanol
M64	dmcdirsynout	outlet of dmc direct synthesis
M65	dmcureasynout	outlet of dmc synthesis from urea
M66	dmcecsynout	outlet of dmc synthesis from ethylene carbonate
M67	dmcpcsynout	outlet of dmc synthesis from propylene carbonate
M68	aasyn1.1out	outlet of aa synthesis reaction 1
M69	aasyn1.2out	outlet of aa synthesis reaction 1 with membrane
M70	aasyn2.1out	outlet of aa synthesis reaction 2
M71	aasyn2.2out	outlet of aa synthesis reaction 2 with membrane
M72	flash6.1top	top product (raw DME) of flash 6.1
M73	flash6.1bottom	bottom product (raw H2O) of flash 6.1
M74	dist6.1out	raw dmc product from dist 6.1
M75	dist6.2top	top product (raw DMC) from dist 6.2
M76	dist6.3top	top product (raw DMC) from dist 6.3
M77	dist6.3bottom	bottom product (raw EG/EC) from dist 6.3
M78	dist6.4top	top product (raw DMC) from dist 6.4
M79	dist6.4bottom	bottom product (raw PG) from dist 6.4
M80	flash6.2out	raw aa product from flash 6.2
M81	flash6.3out	raw aa product (with membrane) from flash 6.3
M82	dist7.2out	raw DMC product from dist 7.2
M83	dist7.3out	raw DMC product from dist 7.3
MeOH	methanol	
H2O	water	
DME	dimethylether	
DMC	dimethylcarbonate	
NH3	ammonia	
EG	ethyleneglycol	
EC	ethylenecarbonate	
PG	propyleneglycol	
FA	formicacid	
SA	succinicacid	
EtOH	ethanol	
CH4	methane	
AA	aceticacid	

Table B.8. Processing steps in database.

StepID	StepName	StepPosition
RM	raw material	1
CM	capture mixing	2
CS1	capture step 1	3
CS2	capture step 2	4
PM	precursor mixing	5
PS	precursor synthesis	6
PS*	precursorsynthesis*	7
M1	mixing 1	8
C1	conversion 1	9
C1*	conversion 1*	10
C1**	conversion 1**	11
P1	purification 1	12
P2	purification 2	13
P3	purification 3	14
P4	purification 4	15
P2M	precursor 2 mixing	16
P2S	precursor 2 synthesis	17
P2P	precursor 2 purification	18
M2	mixing 2	19
C2	conversion 2	20
C2*	conversion 2*	21
P5	purification 5	22
P6	purification 6	23
P7	purification 7	24
PROD	products	25

Table B.9. Intervals and their processing step in the database.

IntervalID	StepID	IntervalType
coalMEACO2	RM	feedstock
coalCO2	RM	feedstock
CapM1	CM	technology
CapABS1	CS1	technology
CapDES1	CS2	technology
preM1	PM	technology
preM2	PM	technology
cr	PS	technology
dr1	PS	technology
dr2	PS*	technology
M1.1	M1	technology
M1.2*	M1	technology
M1.3	M1	technology
M1.4	M1	technology
M1.5	M1	technology
M1.6	M1	technology
meohdirsyn	C1	technology
meohsyn1	C1	technology
meohcosyn	C1	technology
dmedirsyn1	C1	technology
fasyn	C1	technology
sasyn	C1	technology
etohsyn	C1	technology
meohsyn2	C1*	technology
dmedirsyn2	C1*	technology
dmedirsyn3	C1**	technology
flash1.1	P1	technology
flash1.2	P1	technology
flash1.3	P1	technology
dist1.1	P1	technology
flash1.4	P1	technology
reactex1.1	P1	technology
flash1.5	P1	technology
flash1.6	P1	technology
dist2.1	P2	technology
dist2.2	P2	technology
flash2.1	P2	technology

dist2.3	P2	technology
dist2.4	P2	technology
vacdist2.1	P2	technology
memb2.1	P2	technology
flash2.2	P2	technology
dist3.1	P3	technology
dist3.2	P3	technology
dist3.3	P3	technology
dist3.4	P3	technology
crystalizer3.1	P3	technology
dist3.5	P3	technology
dist3.6	P3	technology
dryer4.1	P4	technology
pervap4.1	P4	technology
memb4.1	P4	technology
preM3	P2M	technology
preM4	P2M	technology
preM5	P2M	technology
ureasyn	P2S	technology
ecsyn	P2S	technology
pcsyn	P2S	technology
dist5.1	P2P	technology
dist5.2	P2P	technology
flash5.1	P2P	technology
M2.1	M2	technology
M2.2	M2	technology
M2.3	M2	technology
M2.4	M2	technology
M2.5	M2	technology
M2.6	M2	technology
dmemeohsyn	C2	technology
dmcdirsyn	C2	technology
dmcureasyn	C2	technology
dmcecsyn	C2	technology
dmcpcsyn	C2	technology
aasyn1.1	C2	technology
aasyn1.2	C2	technology
aasyn2.1	C2*	technology
aasyn2.2	C2*	technology

flash6.1	P5	technology
dist6.1	P5	technology
dist6.2	P5	technology
dist6.3	P5	technology
dist6.4	P5	technology
flash6.2	P5	technology
flash6.3	P5	technology
dist7.1	P6	technology
dist7.2	P6	technology
dist7.3	P6	technology
dist7.4	P6	technology
dist7.5	P6	technology
dist7.6	P6	technology
dist7.7	P6	technology
dist8.1	P7	technology
dist8.2	P7	technology
dist8.3	P7	technology
dist8.4	P7	technology
dist8.5	P7	technology
MeOH	PROD	product
H2O	PROD	product
DME	PROD	product
DMC	PROD	product
NH3	PROD	product
EG	PROD	product
EC	PROD	product
PG	PROD	product
FA	PROD	product
SA	PROD	product
EtOH	PROD	product
CH4	PROD	product
AA	PROD	product

B.2 Reaction path synthesis database

The reaction path synthesis database and the statistics are presented in Section 3.2.3.1. In this appendix, further information on the reactions and the database are presented. The targets generated, thermodynamically feasible reactions, the network generated and the reactions with kinetic data are listed.

Table B.10. CAMD targets generated in Step b of RPS.

Smiles		**Group 1**		**Group 2**		**Group 3**	**Group 4**
CO2	1	COO					
H2O	1	H2O					
HH	1	H2					
C=C	1	CH2=CH2					
C#C	1	CH2C					
C=O	1	CH2O					
O=CO	1	HCOOH					
CO	1	CH3	1	OH			
C	1	CH4					
CC	2	CH3					
C(=O)C	1	CH3	1	COH			
O=CC(C)=O	1	CH3CO	1	CHO			
CC(=O)C(O)=O	1	CH3CO	1	COOH			
CO	1	CH3	1	OH			
CC=O	1	CH3	1	CHO			
COC(=O)C	1	CH3	1	CH3COO			
COC=O	1	CH3	1	HCOO			
COC	1	CH3	1	CH3O			
CC(O)=O	1	CH3	1	COOH			
CC(C)=O	1	CH3	1	CH3CO			
CC	2	CH3					
CCC(=O)C=O	1	CH3	1	CH2CO	1	CHO	
CCC(=O)C(O)=O	1	CH3	1	CH2CO	1	COOH	
COC(=O)CO	1	CH3	1	OH	1	CH2COO	
O=CCC(=O)OC	1	CH3	1	CHO	1	CH2COO	
COC(=O)COC(=O)C	1	CH3	1	CH3COO	1	CH2COO	
COCC(=O)OC	1	CH3	1	CH2COO	1	CH3O	
COC(=O)CC(O)=O	1	CH3	1	CH2COO	1	COOH	
COC(=O)CC(C)=O	1	CH3	1	CH3CO	1	CH2COO	
COC(=O)CC	2	CH3	1	CH2COO			
CCOC=O	1	CH3	1	CHO	1	CH2O	

CCOC(O)=O	1	CH3	1	CH2O	1	COOH		
OCC(C)=O	1	CH2	1	OH	1	CH3CO		
O=CCC(C)=O	1	CH2	1	CH3CO	1	CHO		
CC(=O)COC(=O)C	1	CH2	1	CH3CO	1	CH3COO		
O=COCC(C)=O	1	CH2	1	CH3CO	1	HCOO		
COCC(C)=O	1	CH2	1	CH3CO	1	CH3O		
CC(=O)CC(O)=O	1	CH2	1	CH3CO	1	COOH		
CC(=O)CC(C)=O	1	CH2	2	CH3CO				
CCO	1	CH3	1	CH2	1	OH		
CCC=O	1	CH3	1	CH2	1	CHO		
CCOC(=O)C	1	CH3	1	CH2	1	CH3COO		
CCOC	1	CH3	1	CH2	1	CH3O		
CCC(O)=O	1	CH3	1	CH2	1	COOH		
CCC(C)=O	1	CH3	1	CH2	1	CH3CO		
CCC	2	CH3	1	CH2				
CC(O)C(C)=O	1	CH3	1	CH	1	OH	1	CH3CO
O=CC(C)C(C)=O	1	CH3	1	CH	1	CH3CO	1	CHO
O=C(C)OC(C)C(C)=O	1	CH3	1	CH	1	CH3CO	1	CH3COO
O=COC(C)C(C)=O	1	CH3	1	CH	1	CH3CO	1	HCOO
COC(C)C(C)=O	1	CH3	1	CH	1	CH3CO	1	CH3O
CC(=O)C(C)C(O)=O	1	CH3	1	CH	1	CH3CO	1	COOH
CC(=O)C(C)C(C)=O	1	CH3	1	CH	2	CH3CO		
CC(C)O	2	CH3	1	CH	1	OH		
O=CC(C)C	2	CH3	1	CH	1	CHO		
CC(C)OC(=O)C	2	CH3	1	CH	1	CH3COO		
O=COC(C)C	2	CH3	1	CH	1	HCOO		
COC(C)C	2	CH3	1	CH	1	CH3O		
CC(C)C(O)=O	2	CH3	1	CH	1	COOH		
CC(C)C(C)=O	2	CH3	1	CH	1	CH3CO		
CC(C)C	3	CH3	1	CH				
COC(=O)C(=O)OC	2	CH3	2	COO				
COC(=O)CC(=O)OC	2	CH3	1	CH2COO	1	COO		
CCC(=O)CC(=O)OC	2	CH3	1	CH2CO	1	CH2COO		
COC(=O)CCC(=O)OC	2	CH3	2	CH2COO				
CCOCC(=O)OC	2	CH3	1	CH2COO	1	CH2O		
CCC(=O)CO	1	CH3	1	CH2	1	OH	1	CH2CO
CCCC(=O)C=O	1	CH3	1	CH2	1	CH2CO	1	CHO
O=CCC(=O)CC	1	CH3	1	CH2	1	CH2CO	1	CHO
CCC(=O)COC(=O)C	1	CH3	1	CH2	1	CH2CO	1	CH3COO

COCC(=O)CC	1	CH3	1	CH2	1	CH2CO	1	CH3O
CCC(=O)CC(O)=O	1	CH3	1	CH2	1	CH2CO	1	COOH
CCCC(=O)C(O)=O	1	CH3	1	CH2	1	CH2CO	1	COOH
CCC(=O)CC(C)=O	1	CH3	1	CH2	1	CH3CO	1	CH2CO
CCC(=O)CC	2	CH3	1	CH2	1	CH2CO		
CCOC(=O)CO	1	CH3	1	CH2	1	OH	1	CH2COO
OCCC(=O)OC	1	CH3	1	CH2	1	OH	1	CH2COO
OCOC(=O)CC	1	CH3	1	CH2	1	OH	1	CH2COO
CCOC(=O)CC=O	1	CH3	1	CH2	1	CHO	1	CH2COO
O=CCCC(=O)OC	1	CH3	1	CH2	1	CHO	1	CH2COO
O=CCOC(=O)CC	1	CH3	1	CH2	1	CHO	1	CH2COO
CCOC(=O)COC(=O)C	1	CH3	1	CH2	1	CH3COO	1	CH2COO
COC(=O)CCOC(=O)C	1	CH3	1	CH2	1	CH3COO	1	CH2COO
O=COCCC(=O)OC	1	CH3	1	CH2	1	CH2COO	1	HCOO
O=COCOC(=O)CC	1	CH3	1	CH2	1	CH2COO	1	HCOO
CCOC(=O)COC	1	CH3	1	CH2	1	CH2COO	1	CH3O
COCCC(=O)OC	1	CH3	1	CH2	1	CH2COO	1	CH3O
COCOC(=O)CC	1	CH3	1	CH2	1	CH2COO	1	CH3O
CCOC(=O)CC(O)=O	1	CH3	1	CH2	1	CH2COO	1	COOH
COC(=O)CCC(O)=O	1	CH3	1	CH2	1	CH2COO	1	COOH
CCC(=O)OCC(O)=O	1	CH3	1	CH2	1	CH2COO	1	COOH
CCOC(=O)CC(C)=O	1	CH3	1	CH2	1	CH3CO	1	CH2COO
COC(=O)CCC(C)=O	1	CH3	1	CH2	1	CH3CO	1	CH2COO
CCC(=O)OCC(C)=O	1	CH3	1	CH2	1	CH3CO	1	CH2COO
CCOC(=O)CC	2	CH3	1	CH2	1	CH2COO		
CCCC(=O)OC	2	CH3	1	CH2	1	CH2COO		
CCOCO	1	CH3	1	CH2	1	OH	1	CH2O
CCCOC=O	1	CH3	1	CH2	1	CHO	1	CH2O
CCOCC=O	1	CH3	1	CH2	1	CHO	1	CH2O
CCOCOC(=O)C	1	CH3	1	CH2	1	CH3COO	1	CH2O
CCOCOC	1	CH3	1	CH2	1	CH3O	1	CH2O
CCCOC(O)=O	1	CH3	1	CH2	1	CH2O	1	COOH
CCOCC(O)=O	1	CH3	1	CH2	1	CH2O	1	COOH
CCOCC(C)=O	1	CH3	1	CH2	1	CH3CO	1	CH2O
CCOCC	2	CH3	1	CH2	1	CH2O		
OCCO	2	CH2	2	OH				
OCCC=O	2	CH2	1	OH	1	CHO		
O=CCCC=O	2	CH2	2	CHO				
OCCOC(=O)C	2	CH2	1	OH	1	CH3COO		

O=CCCOC(=O)C	2	CH2	1	CHO	1	CH3COO
O=C(C)OCCOC(=O)C	2	CH2	2	CH3COO		
OCCOC=O	2	CH2	1	OH	1	HCOO
O=CCCOC=O	2	CH2	1	CHO	1	HCOO
O=COCCOC(=O)C	2	CH2	1	CH3COO	1	HCOO
O=COCCOC=O	2	CH2	2	HCOO		
OCCOC	2	CH2	1	OH	1	CH3O
O=CCCOC	2	CH2	1	CHO	1	CH3O
COCCOC(=O)C	2	CH2	1	CH3COO	1	CH3O
O=COCCOC	2	CH2	1	HCOO	1	CH3O
COCCOC	2	CH2	2	CH3O		
OCCC(O)=O	2	CH2	1	OH	1	COOH
O=CCCC(O)=O	2	CH2	1	CHO	1	COOH
O=C(C)OCCC(O)=O	2	CH2	1	CH3COO	1	COOH
O=COCCC(O)=O	2	CH2	1	HCOO	1	COOH
COCCC(O)=O	2	CH2	1	CH3O	1	COOH
OC(=O)CCC(O)=O	2	CH2	2	COOH		
OCCC(C)=O	2	CH2	1	OH	1	CH3CO
O=CCCC(C)=O	2	CH2	1	CH3CO	1	CHO
CC(=O)CCOC(=O)C	2	CH2	1	CH3CO	1	CH3COO
O=COCCC(C)=O	2	CH2	1	CH3CO	1	HCOO
COCCC(C)=O	2	CH2	1	CH3CO	1	CH3O
CC(=O)CCC(O)=O	2	CH2	1	CH3CO	1	COOH
CC(=O)CCC(C)=O	2	CH2	2	CH3CO		
CCCO	1	CH3	2	CH2	1	OH
CCCC=O	1	CH3	2	CH2	1	CHO
CCCOC(=O)C	1	CH3	2	CH2	1	CH3COO
CCCOC	1	CH3	2	CH2	1	CH3O
CCCC(O)=O	1	CH3	2	CH2	1	COOH
CCCC(C)=O	1	CH3	2	CH2	1	CH3CO
CCCC	2	CH3	2	CH2		
C=C	1	CH2=CH2				
C#C	1	CH2C				
C=O	1	CH2O				
O=CO	1	HCOOH				
C	1	CH4				
C(=O)C	1	CH3	1	COH		

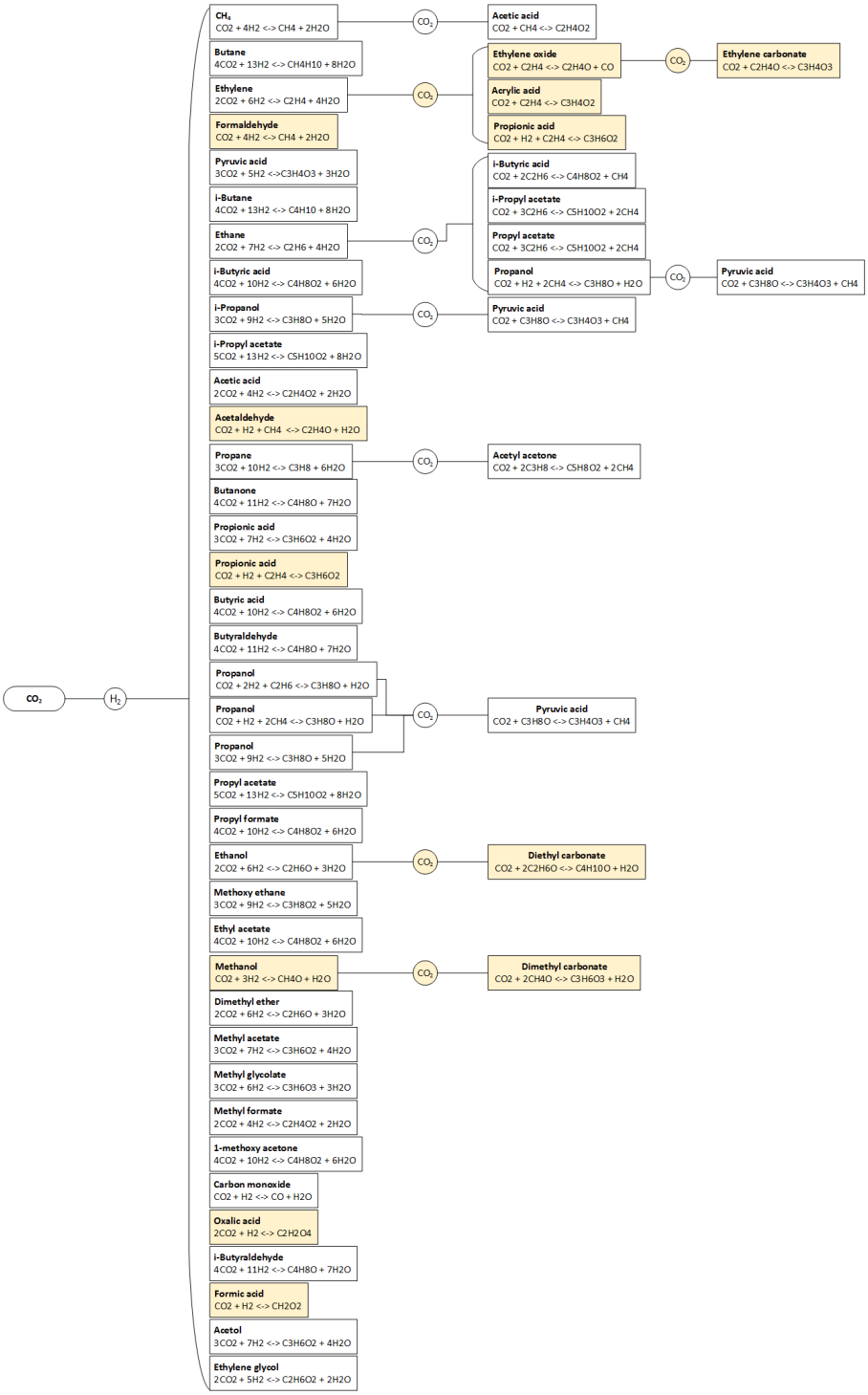


Figure B.1. The first part of the generated reaction tree.

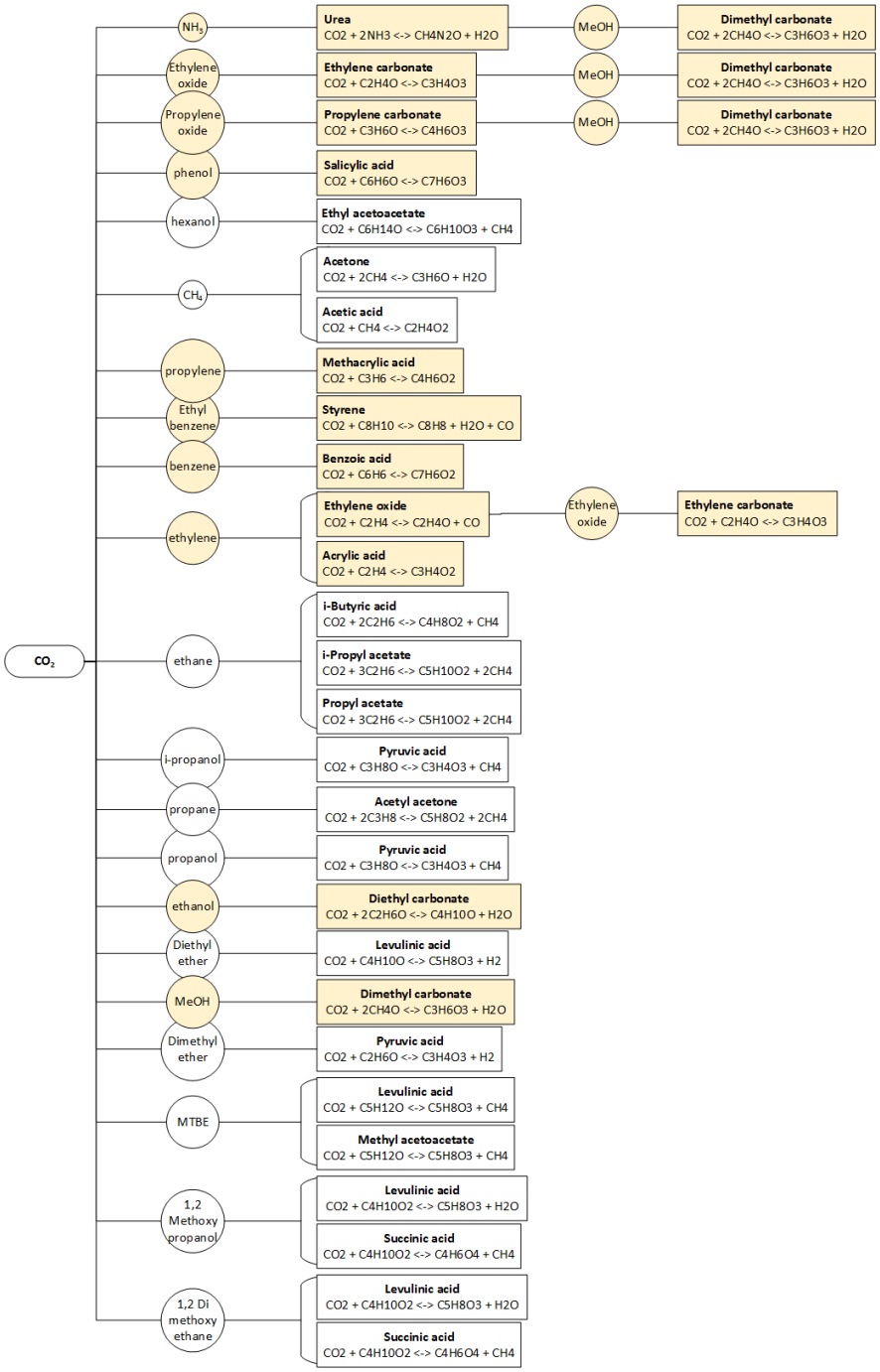


Figure B.2. The second part of the generated reaction tree.

Table B.11. List of the reactions with kinetic data that is also transferred to the superstructure database.

	Unit	Reaction(s)	Temp. (°C)	Pres. (bar)	Cat.	Reference
1	combined reformer	$3CH_4 + 2H_2O + CO_2 \leftrightarrow 4CO + 8H_2$	915	25		Olah et al. (2013)
2 & 3	dry reforming	$CO_2 + CH_4 \leftrightarrow 2CO + 2H_2$; $CO_2 + H_2 \leftrightarrow CO + H_2O$	800	1	Ni/γ-Al_2O_3	Becerra et al. (2003)
4 & 5	methanol direct hydrogenation	$CO_2 + 3H_2 \leftrightarrow CH_4O + H_2O$; $CO_2 + H_2 \leftrightarrow CO + H_2O$	240	60	Cu/ZnO-multi-component	Bussche and Froment (1996)
6 & 7	methanol from syngas (M=2)	$CO + H_2O \leftrightarrow CO_2 + H_2$; $CO_2 + 3H_2 \leftrightarrow CH_4O + H_2O$	240	60	Cu/ZnO-multi-component	Bussche and Froment (1996)
8 & 9	methanol from syngas (M=1)	$CO + 2H_2 \leftrightarrow CH_4O$; $CO + H_2O \leftrightarrow CO_2 + H_2$	220	75	Cu/ZnO-multi-component	Graaf et al. (1988)
10	dimethyl ether	$2CH_4O \leftrightarrow C2H_6O + H_2O$	270	10	Ni/γ-Al_2O_3	Ng et al. (1999)
11, 12 & 13	dimethyl ether from syngas (M=1)	$CO + H_2O \leftrightarrow CO_2 + H_2$; $CO + 2H_2 \leftrightarrow CH_4O$; $2CH_4O \leftrightarrow C2H_6O + H_2O$	250	50	Cu/ZnO/ Al_2O_3 + γ-Al_2O_3	Ng et al. (1999)
14	urea synthesis	$CO_2 + 2NH_3 \leftrightarrow CH_4N_2O + H_2O$	190	160		Isla et al. (1993)
15	ethylene carbonate synthesis	$CO_2 + C_2H_4O \leftrightarrow C_3H_4O_3$	110	40	ionic liquid	Dai et al. (2009)
16	propylene carbonate synthesis	$CO_2 + C_3H_6O \leftrightarrow C_4H_6O_3$	100	7.9	ionic liquid	Park et al. (2004)

17	dimethyl carbonate synthesis	$CO_2 + 2CH_4O \leftrightarrow C_3H_6O_3 + H_2O$	150	50	CeO_2	Kuenen et al. (2016b,a)
18	dimethyl carbonate via urea synthesis	$CH_4N_2O + 2CH_4O \leftrightarrow C_3H_6O_3 + 2NH_3$	140	8	ionic liquid	Wang et al. (2009)
19	dimethyl carbonate via EC synthesis	$C_3H_4O_3 + 2CH_4O \leftrightarrow C_3H_6O_3 + C_2H_6O_2$	160	10	immobilized ionic liquid	Kim et al. (2010)
20	dimethyl carbonate via PC synthesis	$C_4H_6O_3 + 2CH_4O \leftrightarrow C_3H_6O_3 + C_3H_8O_2$	40	1	homogeneous CH_3NaO	Holtbruegge et al. (2013)
21	formic acid synthesis	$CO_2 + H_2 \leftrightarrow CHOOH$	90	80	homogeneous Ru	Moret et al. (2014)
22, 23, 24 & 25	succinic acid via fermentation	$C_6H_{12}O_6 + 2CO_2 + 4H \leftrightarrow C_4H_6O_4 + H_2O$; $C_6H_{12}O_6 \leftrightarrow 3CH_3OOH$; $C_6H_{12}O_6 \leftrightarrow 2C_3H_4O_3 + 4H$; $C_6H12O_6 + 2CO_2 \leftrightarrow C_4H_6O_5$	37	1.5	M. succinici-producens	Vaswani (201)

26 - 35		ethanol synthesis	$2CO_2 + 6H_2 \leftrightarrow CH_3CH_2OH + 3H_2O$; $3CO_2 + 7H_2 \leftrightarrow C_3H_6O_2 + 4H_2O$; $CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$; $2CO_2 + 7H_2 \leftrightarrow C_2H_6 + 4H_2O$; $4CO_2 + 13H_2 \leftrightarrow C_4H_{10} + 8H_2O$; $3CO_2 + 7H_2 \leftrightarrow C_3H_8 + 6H_2O$; $3CO_2 + 9H_2 \leftrightarrow C_3H_8O + 5H_2O$; $CO_2 + 3H_2 \leftrightarrow CH_4O + H_2O$; $4CO_2 + 12H_2 \leftrightarrow C_4H_{10}O + 7H_2O$; $CO_2 + H_2 \leftrightarrow CO + H_2O$	240	50	Rh-Li/SiO_2	Kusama et al. (1997)
36 & 37		acetic acid synthesis	$2CH_4O + CO \leftrightarrow C_3H_6O_2 + H_2O$; $C_3H_6O_2 + H_2O \leftrightarrow CH_3COOH + CH_4O$	190	30	Ni-active carbon	Omata et al. (1985)	

B.3 Simulation library

This work contains a large number of simulations done in the various simulation tools. In order to organize these, they have been collected in a simulation library. This library contains all simulations related to capture and conversion processes. They are organized by product and whether capture is considered or not. Then, the various simulations are organized by base case or any other special features. In addition, the software and version that is used is stated so that the reuse of the simulations is simplified. Currently, the simulation has simulations covering the products listed in Table B.12. Additionally, a detailed list of the simulations is provided in Table B.13.

Table B.12. The statistics of the simulation library of carbon dioxide capture and utilization processes.

Type	Product	Simulations	Description
Carbon capture (CC)	Carbon dioxide	27	Simulations in various versions of ProII capturing carbon dioxide from flue gas from a coal-fired power plant and in natural gas sweetening; considers various concentrations and optimizations
CO_2 utilization and CCU	Methanol	20	Simulations in AspenPlus and ProII taking carbon dioxide to methanol via different route; considers various optimization alternatives and some are integrated with carbon capture via MEA absorption
CO_2 utilization and CCU	Dimethyl ether (DME)	13	Simulations in AspenPlus and ProII taking carbon dioxide to dimethyl ether via different synthesis routes (via methanol or directly from syngas); considers various optimization alternatives and some are integrated with carbon capture via MEA absorption
CO_2 utilization and CCU	Dimethyl carbonate (DMC)	12	Simulations in AspenPlus and ProII taking carbon dioxide to dimethyl carbonate via different routes (ethylene carbonate, direct, etc.) and considering methanol production or purchase; some are also intensified alternatives and some are integrated with carbon capture via MEA absorption
CO_2 utilization and CCU	Formic acid	6	Simulations in ProII capturing and converting carbon dioxide to formic acid with some optimization
CO_2 utilization	Succinic acid	1	Simulation in AspenPlus taking carbon dioxide to succinic acid
CO_2 utilization	Acetic acid	9	Simulations in AspenPlus taking carbon dioxide to acetic acid considering different routes and optimization options

Table B.13. The simulation library.

Type	Title	CO_2 source	Product	Route	Software	Author
capture	CC_ref_ v9.2	coal-fired flue gas	CO_2 (99 mol%)	MEA capture	ProII V9.2	Fjellerup
capture	CC_ref_ v9.3	coal-fired flue gas	CO_2 (99 mol%)	MEA capture	ProII V9.3	Fjellerup
capture	CC_opt_ v9.2	coal-fired flue gas	CO_2 (97.2 mol%)	MEA capture	ProII V9.2	Fjellerup
capture	CC_opt_ v9.3	coal-fired flue gas	CO_2 (97.2 mol%)	MEA capture	ProII V9.3	Fjellerup
capture & conversion	CCU_MeOH_ v9.2	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.2	Fjellerup
capture & conversion	CCU_MeOH_ v9.3	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Fjellerup
capture & conversion	CCU_FA_ basecase_ v9.2	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.2	Fjellerup
capture & conversion	CCU_FA_ basecase_ v9.3	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.3	Fjellerup
capture & conversion	CCU_FA_ extDist_ v9.2	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.2	Fjellerup

capture & conversion	CCU_FA_ extDist_ v9.3	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.3	Fjellerup
capture & conversion	CCU_FA_ optDist_ v9.2	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.2	Fjellerup
capture & conversion	CCU_FA_ optDist_ v9.3	coal-fired flue gas	Formic acid (95 wt%)	MEA capture and hydrogenation	ProII V9.3	Fjellerup
conversion	AA_DR_ basecase	CO_2	Acetic Acid	dry reforming, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_DR_ compopt	CO_2	Acetic Acid	dry reforming, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_DR_ heatint	CO_2	Acetic Acid	dry reforming, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_ DRmemb_ basecase	CO_2	Acetic Acid	dry reforming with membrane, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_ DRmemb_ compopt	CO_2	Acetic Acid	dry reforming with membrane, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_ DRmemb_ heatint	CO_2	Acetic Acid	dry reforming with membrane, methanol synthesis and carbonylation	Aspen V8.6	Prasertsri

conversion	AA_ meohdir_ basecase	CO_2	Acetic Acid	direct hydrogenation and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_ meohdir_ compopt	CO_2	Acetic Acid	direct hydrogenation and carbonylation	Aspen V8.6	Prasertsri
conversion	AA_ meohdir_ heatint	CO_2	Acetic Acid	direct hydrogenation and carbonylation	Aspen V8.6	Prasertsri
capture	CC_NG_ref_ v8.2	natural gas	CO_2 (99%)	MEA capture	ProII V8.2	Godfroy
capture	CC_NG_ref_ v8.3	natural gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_NG_ref_ v9.3	natural gas	CO_2 (99%)	MEA capture	ProII V9.3	Godfroy
capture	CC_NG_+6	natural gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_NG_+12	natural gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_NG_PZ	natural gas	CO_2 (99%)	PZ capture	ProII V8.3	Godfroy
capture	CC_NG_ RR0.25	natural gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_CF_ref_ v8.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_CF_ref_ v9.2	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V9.3	Godfroy
capture	CC_CF_ref_ v9.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V9.3	Godfroy

capture	CC_CF_+6_ v8.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_CF_+6_ v9.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V9.3	Godfroy
capture	CC_CF_+12_ v8.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V8.3	Godfroy
capture	CC_CF_+12_ v9.3	coal-fired flue gas	CO_2 (99%)	MEA capture	ProII V9.3	Godfroy
capture	CC_CF_AMP_ v8.3	coal-fired flue gas	CO_2 (99%)	AMP capture	ProII V8.3	Godfroy
capture	CC_CF_AMP_ v9.3	coal-fired flue gas	CO_2 (99%)	AMP capture	ProII V9.3	Godfroy
capture	CC_CF_PZ_ v8.3	coal-fired flue gas	CO_2 (99%)	PZ capture	ProII V8.3	Godfroy
capture	CC_CF_PZ_ v9.3	coal-fired flue gas	CO_2 (99%)	PZ capture	ProII V9.3	Godfroy
capture	CC_CF_DEA_ v8.3	coal-fired flue gas	CO_2 (99%)	DEA capture	ProII V8.3	Godfroy
capture	CC_CF_DEA_ v9.3	coal-fired flue gas	CO_2 (99%)	DEA capture	ProII V9.3	Godfroy

synthesis	DMC_PC_ basecase	N/A	DMC & PG	DMC synthesis via propylene carbonate	Aspen V8.6	Babi
synthesis	DMC_PC_ pervap	N/A	DMC & PG	DMC synthesis via propylene carbonate	Aspen V8.6	Babi
synthesis	DMC_PC_ reactdist	N/A	DMC & PG	DMC synthesis via propylene carbonate	Aspen V8.6	Babi
conversion	DMC_ dirsyn_ basecase	CO_2	DMC & PG	DMC synthesis via propylene carbonate	Aspen V8.6	Calvera
conversion	MeOH_dir_ basecase_ scaled	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Calvera
conversion	PC_ basecase_ scaled	CO_2	PC	carbonate synthesis	ProII V9.3	Calvera
synthesis	DMC_ PCMeOH_ basecase_ scaled	N/A	DMC & PG	DMC synthesis via propylene carbonate	Aspen V8.6	Calvera
conversion	DMC_EC_ basecase	CO_2	DMC, EC, EG	DMC synthesis via ethylene carbonate	Aspen V8.8	Kongpanna
conversion	DMC_Urea_ basecase	CO_2	DMC	DMC synthesis via urea	Aspen V8.8	Kongpanna
conversion	DMC_EC_RD	CO_2	DMC, EC, EG	DMC synthesis via ethylene carbonate		Kongpanna
conversion	DMC_Urea_ RD	CO_2	DMC	DMC synthesis via urea	Aspen V8.6	Kongpanna
conversion	DMC_Urea_ pervap NH3removal	CO_2	DMC	DMC synthesis via urea	Aspen V8.6	Kongpanna
conversion	DMC_Urea_ pervap	CO_2	DMC	DMC synthesis via urea		Kongpanna

conversion	DME_DR_ basecase	CO_2	DME	DME synthesis via methanol from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_DR_ compopt	CO_2	DME	DME synthesis via methanol from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_DR_ heatint	CO_2	DME	DME synthesis via methanol from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_DR_ MeOHpur	CO_2	DME	DME synthesis via methanol from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_ meohdir_ basecase	CO_2	DME	DME synthesis via methanol from direct hydrogenation	Aspen V8.6	Prasertsri
conversion	DME_ meohdir_ heatint	CO_2	DME	DME synthesis via methanol from direct hydrogenation	Aspen V8.6	Prasertsri
conversion	DME_ meohdir_ wastepur	CO_2	DME	DME synthesis via methanol from direct hydrogenation	Aspen V8.6	Prasertsri
conversion	DME_ dirsyn_ basecase	CO_2	DME	DME synthesis via syngas from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_ dirsyn_ heatint	CO_2	DME	DME synthesis via syngas from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_ dirsyn_ memb	CO_2	DME	DME synthesis via syngas from dry reforming	Aspen V8.6	Prasertsri
conversion	DME_ dirsyn_ wastepur	CO_2	DME	DME synthesis via syngas from dry reforming	Aspen V8.6	Prasertsri

conversion	PC_basecase	CO_2	PC	carbonate synthesis	ProII V9.3	Calvera
conversion	SA_glucose_ basecase	CO_2	SA	succinic acid via glucose fermentation	Aspen V8.6	Calvera
conversion	MeOH_SR_ basecase	N/A	MeOH	methanol via steam reforming	Aspen V8.6	Roh
conversion	MeOH_CR_ basecase2	CO_2	MeOH	methanol via combined reforming	Aspen V8.6	Roh
conversion	MeOH_CR_ basecase	CO_2	MeOH	methanol via combined reforming	Aspen V8.6	Nguyen
conversion	MeOH_CR_opt	CO_2	MeOH	methanol via combined reforming	Aspen V8.6	Nguyen
conversion	MeOH_CR_alt	CO_2	MeOH	methanol via combined reforming	Aspen V8.6	Nguyen
conversion	MeOH_dir_ basecase	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Nguyen
conversion	MeOH_dir_opt	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Nguyen
conversion	MeOH_TR_ basecase	CO_2	MeOH	methanol via tri-reforming	Aspen V8.6	Nguyen
conversion	MeOH_TR_opt	CO_2	MeOH	methanol via tri-reforming	Aspen V8.6	Nguyen
conversion	MeOH_TR_alt	CO_2	MeOH	methanol via tri-reforming	Aspen V8.6	Nguyen
capture & conversion	CCU_MeOH_ basecase2	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Mads
capture & conversion	CCU_MeOH_ Alt1	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Mads

capture & conversion	CCU_MeOH_ Alt2	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Mads
capture & conversion	CCU_MeOH_ Alt3	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Mads
capture & conversion	CCU_MeOH_ Alt4	coal-fired flue gas	MeOH	MEA capture and direct hydrogenation	ProII V9.3	Mads
conversion	MeOH_dir_ im-pureCO2H2	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Frauzem
conversion	MeOH_dir_ pureCO2H2	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Frauzem
conversion	MeOH_dir_ impureCO2 pureH2	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Frauzem
conversion	MeOH_dir_ pureCO2 impureH2	CO_2	MeOH	direct hydrogenation	Aspen V8.6	Frauzem
capture & conversion	DME_ meo-hdirsyn	coal-fired flue gas	DME	MEA capture, direct hydrogenation and DME synthesis	ProII V9.3	Frauzem
capture & conversion	DME_meohcr	coal-fired flue gas	DME	MEA capture, methanol from combined reforming and DME synthesis	ProII V9.3	Frauzem
capture & conversion	DMC_EC_ meohdirsyn	coal-fired flue gas	DMC & EG	MEA capture, direct hydrogenation, DMC via ethylene carbonate	ProII V9.3	Frauzem

capture & conversion	DMC_EC_ meohcr	coal-fired flue gas	DMC & EG	MEA capture, methanol from combined reforming and DMC via ethylene carbonate	ProII V9.3	Frauzem

Appendix C

Super-O

As has been mentioned in Section 3.2.4, the software interface, Super-O, is used in the framework to facilitate the implementation of certain steps in Stage 1. The different functions of the interface and their interaction are shown in Figure

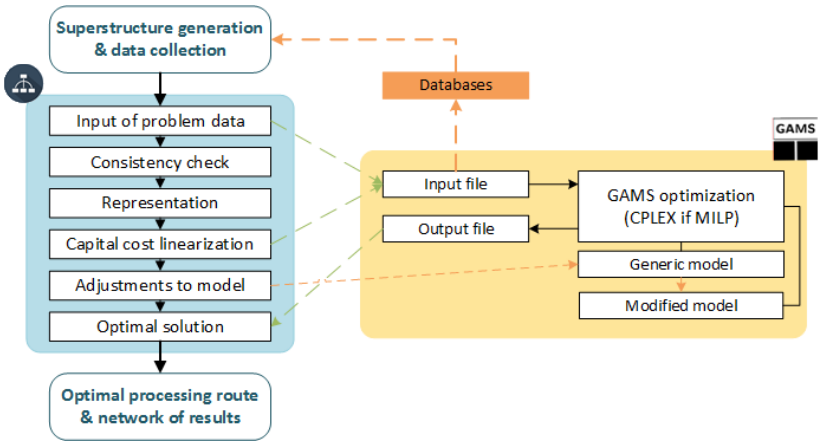


Figure C.1. The visual representation of the steps in Super-O and the interaction between Super-O and the other tools. The dashed orange lines are manual actions and the dashed green lines are automated in the interface. (adapted from Bertran et al. (2017))

Further details on Super-O are presented in the Supplementary Material of the paper *A generic methodology for processing route synthesis and design based on superstructure optimization* (Bertran et al., 2017).

Appendix D

Stage 2 results

The important results of Stage 2 are presented in Section 4.2. In this appendix, further details are provided on the individual process parts (carbon dioxide capture, methanol synthesis, dimethyl ether synthesis, ethylene carbonate synthesis and dimethyl carbonate synthesis) and the integrated processes (CCU to dimethyl ether and dimethyl carbonate).

D.1 Carbon dioxide capture

Carbon dioxide capture is designed as a monoethyl amine (MEA) absorption process, which is currently the industrial standard (Wilcox, 2012). This process consists of 4 units: an absorber, a desorber, a heater to the desorber column and a cooler to the absorber column. This process is applied to the removal of carbon dioxide from flue gas from a coal-fired power plant. The amount of flue gas entering the process is fixed to 4.5 million tons per year and 1 million tons per year of carbon dioxide, which is the amount for a traditional 150MW coal-fired power plant. The equipment is designed using traditional design methods. The flowsheet of this part is shown in Figure D.1 with the resulting stream table also provided (Table D.1).

Traditionally, the desorber column has high reboiler duties in order to remove the carbon dioxide from the solvent at a high purity (99.9 mol%). To address this, the process has been optimized by reducing the purity of the recovered carbon dioxide (Fjellerup, 2015) to 97.2 mol%. The optimized process is the analyzed for economic and environmental parameters using the tools ECON (Saengwirun, 2011) and LCSoft (Kalakul et al., 2014). The results show that the utility costs, equipment costs and carbon footprint are all decreased. the utility cost is decreased by almost 90%, the equipment cost is reduced by 28% and the carbon footprint becomes negative (more carbon dioxide is captured than emitted via utilities).

Table D.1. The stream table of the simulation shown in Figure D.1.

Stream Name		S01	S12	S2	S3	S31	S32	S4
Stream Description		Flue gas 1	Rich solvent			CO2-PRODUCT	Solvent recycle 1	Solvent recyccle 2
Stream Phase		Vapor	Liquid	Mixed	Vapor	Vapor	Liquid	Liquid
Total Molar Rate	kg-mol/hr	18828.000	52433.379	52433.379	15895.216	3033.776	49399.603	49399.603
Total Mass Rate	kg/hr	561733.866	1724673.638	1724673.638	432617.563	131370.319	1593303.391	1593303.391
Total Molecular Weight		29.835	32.893	32.893	27.217	43.303	32.253	32.253
Temperature	C	47.343	76.134	110.850	50.724	25.132	124.983	46.000
Pressure	BAR	1.567	1.580	1.580	1.010	1.210	1.778	1.778
Total Molar Comp. Fractions								
N2		0.7740	0.0001	0.0001	0.9166	0.0013	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.1570	0.1103	0.1103	0.0004	0.9723	0.0574	0.0574
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0690	0.6108	0.6108	0.0824	0.0264	0.6467	0.6467
MEA		0.0000	0.2788	0.2788	0.0006	0.0000	0.2960	0.2960
Total Weight Comp. Fractions								
N2		0.7267	0.0001	0.0001	0.9434	0.0009	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.2316	0.1476	0.1476	0.0006	0.9882	0.0783	0.0783
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0417	0.3345	0.3345	0.0546	0.0110	0.3612	0.3612
MEA		0.0000	0.5178	0.5178	0.0014	0.0000	0.5605	0.5605

Stream Name		S5	S7	S81	S82	S91	S92
Stream Description		Solvent recycle 3		MEA Make-up		Water Make-up	
Stream Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Total Molar Rate	kg-mol/hr	49399.603	49500.595	10.098	3599989.902	90.905	3599909.095
Total Mass Rate	kg/hr	1593303.391	1595557.335	616.794	219900779.385	1637.680	64853369.492
Total Molecular Weight		32.253	32.233	61.084	61.084	18.015	18.015
Temperature	C	46.000	46.010	46.000	46.000	46.850	46.850
Pressure	BAR	1.013	1.013	1.013	1.013	1.013	1.013
Total Molar Comp. Fractions							
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0574	0.0573	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.6467	0.6472	0.0000	0.0000	1.0000	1.0000
MEA		0.2960	0.2956	1.0000	1.0000	0.0000	0.0000
Total Weight Comp. Fractions							
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0783	0.0782	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.3612	0.3617	0.0000	0.0000	1.0000	1.0000
MEA		0.5605	0.5601	1.0000	1.0000	0.0000	0.0000

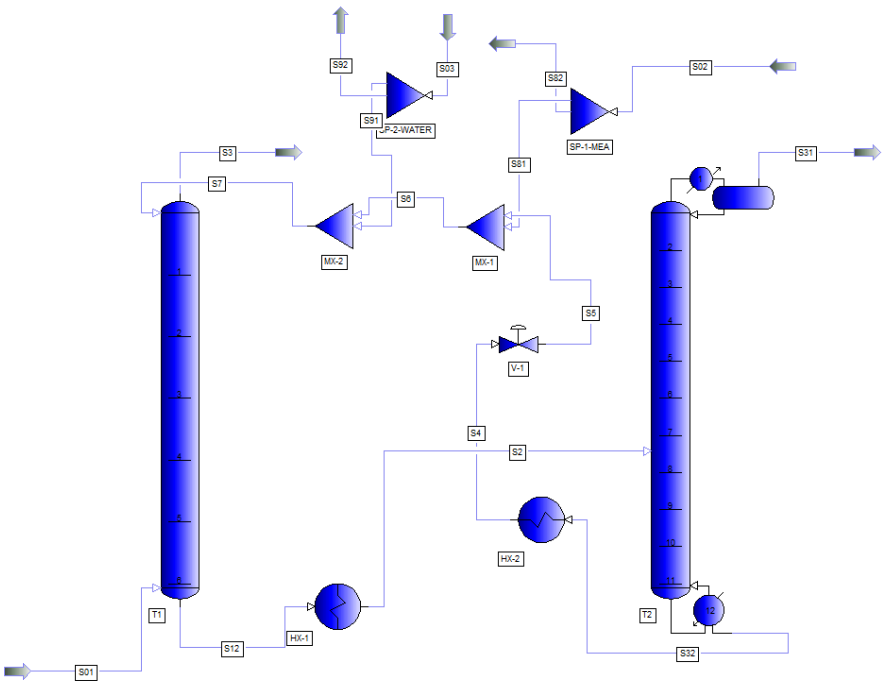


Figure D.1. The flowsheet of the simulation for the capture process (adapted from Fjellerup (2015)).

D.2 Methanol synthesis via combined reforming

Traditionally, methanol is synthesized via a 2-step process, where natural gas (or coal) is reformed to produce syngas and then this syngas is converted to methanol. However, this 2-step process is associated with high emissions. An alternative to this is combined reforming, which combines dry reforming and steam reforming. Combined reforming, also known as bi-reforming, is able to provide the syngas at the desired ration (M=2) for methanol synthesis (Olah et al., 2013). The combined reforming process is designed and simulated in Pro II, as shown in Figure D.2 with the stream results listed in Table D.2.

The process consists of two reactors, compressors, a flash and two distillation columns. The combined reforming and methanol synthesis reaction conditions were optimized in the work of Roh et al. (2016b). The compressors considered are multi-stage compressors with intercooling for the carbon dioxide. The steam is assumed to come from a pipeline at the necessary pressure. After the combined reforming reaction, the gases are compressed to the necessary pressure for the methanol synthesis reaction. The methanol synthesis reaction is modeled using

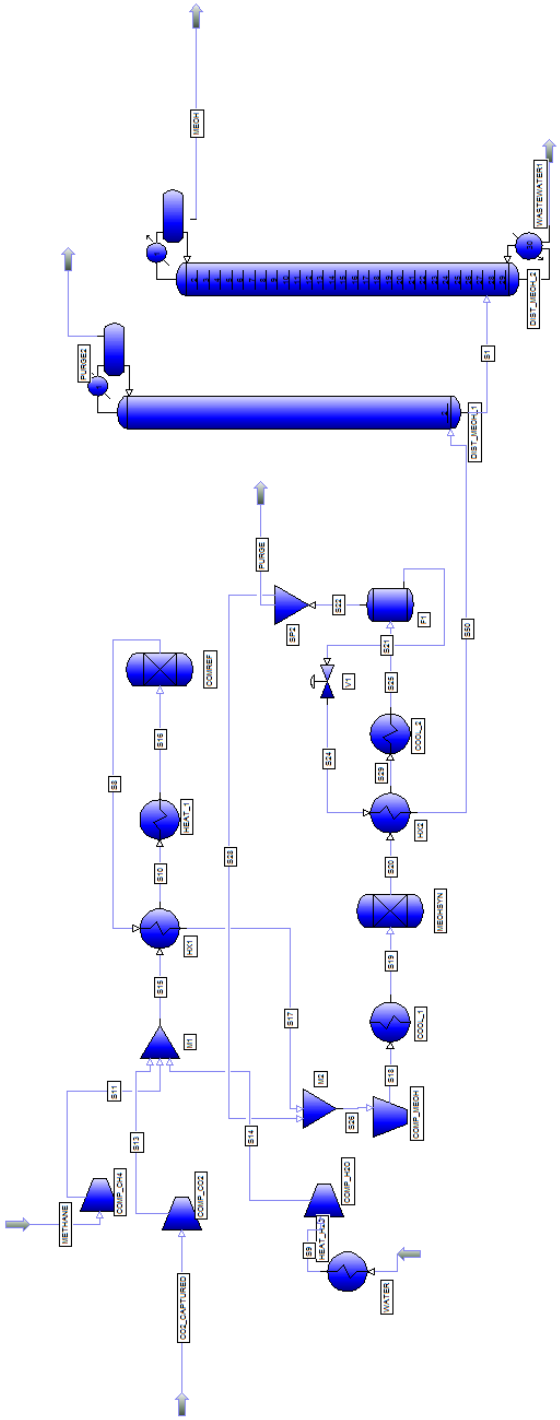
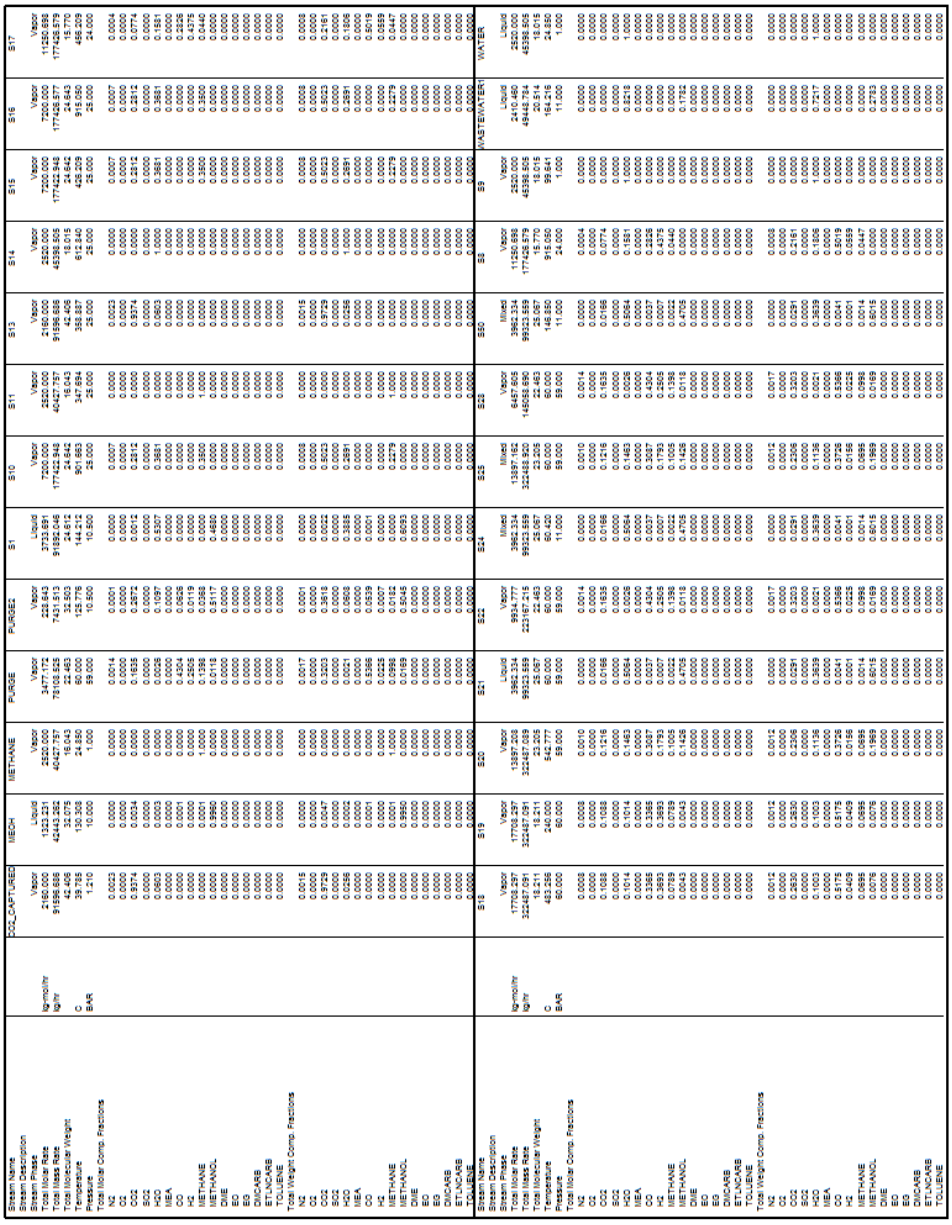


Figure D.2. The flowsheet of the simulation for the methanol from combined reforming process (adapted from Roh et al. (2016b)).

Table D.2. The stream table of the simulation for methanol synthesis via combined reforming shown in Figure D.2.



a LHHW model (Bussche and Froment, 1996). The raw methanol is first flashed to remove the light components, which are recycled. Then, a two-step distillation is used to achieve the desired high-purity methanol (99.95 mol%). In addition, heat integration is performed to make use of the temperature differences throughout the process. This process is simulated and analyzed.

From the analysis, the economics and environmental performance are evaluated. For the 400000 tons per year needed for dimethyl carbonate synthesis and dimethyl ether synthesis, the capital cost is 209.3 million USD and the operating cost is 205.7 million USD per year. The majority of the costs in this section come from the compression and the second distillation column. Also, the NetCO_2 of this part of the process is 0.55 kg_{CO_2}/kg_{MeOH}, which is positive, though less than the traditional route.

D.3 Methanol synthesis via direct hydrogenation

Alternatively to combined reforming, methanol can synthesized from carbon dioxide directly via hydrogenation. In direct hydrogenation, the carbon dioxide is reacted with hydrogen to produce methanol. The entire process is shown in Figure D.3 with the streams shown in Table D.3.

First, the hydrogen and carbon dioxide are compressed using multi-stage commpressors with intercooling. The conditions of the reaction are the same as the methanol synthesis via syngas as described in combined reforming. The reaction is again modeled by the LHHW kinetic model (Bussche and Froment, 1996). The conversion of the reaction is lower compared to when syngas is used as the feed. However, the product can be flashed and recycled to obtain an overall conversion of 0.8 for carbon dioxide. Again, two distillation columns are used to obtain the methanol at the desired purity.

From the economic and environmental analysis, the capital and operating costs for the production of 400000 tons per year are 257.4 million USD and 233.9 million USD per year, respectively. The majority of the operating and capital costs of this section are from the methanol distillation and the compression of carbon dioxide and hydrogen. Also, the NetCO_2 is -0.45 kg_{CO_2}/kg_{MeOH}. This route is therefore, net carbon dioxide reducing (converts more carbon dioxide than is emitted indirectly).

D.4 Dimethyl ether synthesis

Dimethyl ether is synthesized from methanol. The reactor is modeled using a LHHW kinetic model (Ng et al., 1999). The operating conditions have been previously

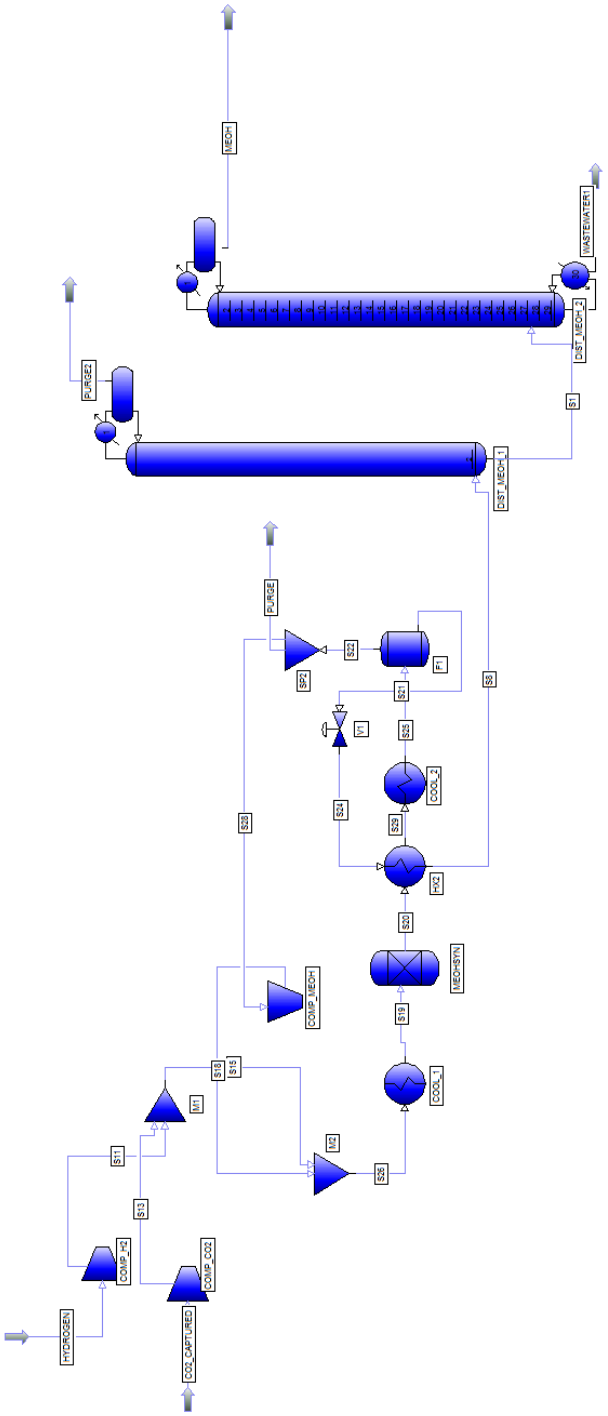


Figure D.3. The flowsheet of the simulation for the methanol via direct hydrogenation process (adapted from Roh et al. (2016b)).

Table D.3. The stream table of the simulation for methanol synthesis via direct hydrogenation shown in Figure D.3.

Stream Name	CO2_CAPTURED		HYDROGEN		MEOH		PURGE		PURGE2		S1		S11		S13		S15		S18	
Stream Description																				
Stream Phase	Vapor		Vapor		Liquid		Vapor		Vapor		Liquid		Vapor		Vapor		Vapor		Vapor	
Total Molar Rate	2160.000	kgmol/hr	6048.000	kgmol/hr	1449.767	kgmol/hr	2006.568	kgmol/hr	75.299	kgmol/hr	3565.862	kgmol/hr	6048.000	kgmol/hr	2160.000	kgmol/hr	8208.000	kgmol/hr	18059.166	kgmol/hr
Total Mass Rate	93333.560	kg/hr	12192.043	kg/hr	46475.442	kg/hr	27489.463	kg/hr	2629.763	kg/hr	75912.515	kg/hr	12192.043	kg/hr	93333.560	kg/hr	105725.603	kg/hr	247407.466	kg/hr
Total Molecular Weight	43.203		2.016		32.057		13.700		34.924		21.293		2.016		43.203		12.881		13.700	
Temperature	25.152	C	24.850	C	131.999	C	50.000	C	120.461	C	144.434	C	582.343	C	332.801	C	488.426	C	168.935	C
Pressure	1.210	BAR	1.000	BAR	10.000	BAR	24.000	BAR	10.500	BAR	10.500	BAR	25.000	BAR	25.000	BAR	25.000	BAR	60.000	BAR
Total Molar Comp. Fractions																				
N2	0.0013		0.0000		0.0000		0.0014		0.0001		0.0000		0.0000		0.0013		0.0003		0.0014	
O2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO2	0.9723		0.0000		0.0032		0.2833		0.4233		0.0015		0.0000		0.9723		0.2559		0.2533	
SO2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
H2O	0.0254		0.0000		0.0018		0.0627		0.0892		0.5217		0.0000		0.0254		0.0569		0.0057	
MEA	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO	0.0099		0.0000		0.0000		0.0099		0.0015		0.0000		0.0000		0.0000		0.0000		0.0099	
H2	0.1077		1.0000		0.0000		0.1077		0.0310		0.0000		0.0000		0.0000		0.7388		0.1077	
METHANE	0.0000		0.0000		0.9950		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
METHANOL	0.0000		0.0000		0.9950		0.0219		0.4650		0.4758		0.0000		0.0000		0.0000		0.0219	
DME	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
DMCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
ET_LNCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
TOLUENE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
Total Weight Comp. Fractions																				
N2	0.0029		0.0000		0.0000		0.0029		0.0001		0.0000		0.0000		0.0029		0.0008		0.0029	
O2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO2	0.9882		0.0000		0.0044		0.8138		0.9334		0.0027		0.0000		0.9882		0.8742		0.8138	
SO2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
H2O	0.0110		0.0000		0.0010		0.0075		0.0460		0.3798		0.0000		0.0110		0.0097		0.0075	
MEA	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO	0.0023		0.0000		0.0000		0.0023		0.0003		0.0000		0.0000		0.0023		0.0003		0.0023	
H2	0.1153		1.0000		0.0000		0.1041		0.0018		0.0000		1.0000		0.0000		0.1153		0.1041	
METHANE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
METHANOL	0.0913		0.0000		0.9946		0.0913		0.4774		0.8174		0.0000		0.0913		0.0000		0.0913	
DME	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
DMCARB	0.0001		0.0000		0.0001		0.0001		0.0001		0.0001		0.0000		0.0001		0.0001		0.0001	
ET_LNCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
TOLUENE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	

Stream Name	S19		S20		S21		S24		S25		S26		S29		S8		WASTEWATER	
Stream Description																		
Stream Phase	Vapor		Liquid		Liquid		Mixed		Mixed		Vapor		Vapor		Mixed		Liquid	
Total Molar Rate	23997.720	kgmol/hr	3131.161	kgmol/hr	3131.161	kgmol/hr	23196.746	kgmol/hr	23196.746	kgmol/hr	26327.166	kgmol/hr	18069.109	kgmol/hr	23196.746	kgmol/hr	3131.161	kgmol/hr	1606.096	kgmol/hr
Total Mass Rate	353134.075	kg/hr	78242.277	kg/hr	78242.277	kg/hr	353133.988	kg/hr	353133.988	kg/hr	353133.988	kg/hr	247405.199	kg/hr	353133.988	kg/hr	78242.277	kg/hr	29137.073	kg/hr
Total Molecular Weight	14.714		24.988		24.988		15.222		15.222		13.414		13.695		15.222		24.988		18.145	
Temperature	346.629	C	60.000	C	60.000	C	60.326	C	60.000	C	268.979	C	305.880	C	146.859	C	182.597	C	182.597	C
Pressure	24.000	BAR	24.000	BAR	11.000	BAR	11.000	BAR	24.000	BAR	24.000	BAR	24.000	BAR	11.000	BAR	11.000	BAR	11.000	BAR
Total Molar Comp. Fractions																				
N2	0.0011		0.0000		0.0000		0.0012		0.0012		0.0011		0.0014		0.0012		0.0000		0.0000	
O2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO2	0.2541		0.0000		0.0116		0.2207		0.2207		0.2541		0.2533		0.2207		0.0116		0.0000	
SO2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
H2O	0.0061		0.0739		0.5113		0.0739		0.0739		0.0061		0.0057		0.0739		0.5113		0.9910	
MEA	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO	0.0008		0.0000		0.0000		0.0025		0.0025		0.0008		0.0008		0.0025		0.0000		0.0000	
H2	0.7168		0.8133		0.0000		0.8133		0.8133		0.7168		0.7059		0.8133		0.0000		0.0000	
METHANE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
METHANOL	0.0151		0.0833		0.4763		0.0833		0.0833		0.0151		0.0219		0.0833		0.4763		0.0090	
DME	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
DMCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
ET_LNCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
TOLUENE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
Total Weight Comp. Fractions																				
N2	0.0023		0.0000		0.0000		0.0023		0.0023		0.0023		0.0029		0.0023		0.0000		0.0000	
O2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO2	0.8319		0.0000		0.0205		0.8381		0.8381		0.8319		0.8138		0.8381		0.0205		0.0000	
SO2	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
H2O	0.0031		0.3686		0.9875		0.3686		0.3686		0.0031		0.0031		0.3686		0.9875		0.9841	
MEA	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
CO	0.0142		0.0158		0.0000		0.0158		0.0158		0.0142		0.0203		0.0158		0.0000		0.0000	
H2	0.1075		0.0811		0.0001		0.0811		0.0811		0.1075		0.1041		0.0811		0.0001		0.0000	
METHANE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
METHANOL	0.0359		0.1752		0.8107		0.1752		0.1752		0.0359		0.0513		0.1752		0.8107		0.0159	
DME	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
E0	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
DMCARB	0.0001		0.0001		0.0001		0.0001		0.0001		0.0001		0.0001		0.0001		0.0001		0.0000	
ET_LNCARB	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	
TOLUENE	0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000		0.0000	

optimized by Prasertsri et al. (2016). Subsequently, the dimethyl ether is easily purified using distillation, as there are no azeotropes. The entire flowsheet from the simulation is shown in Figure D.4 and the stream information provided in Table D.4.

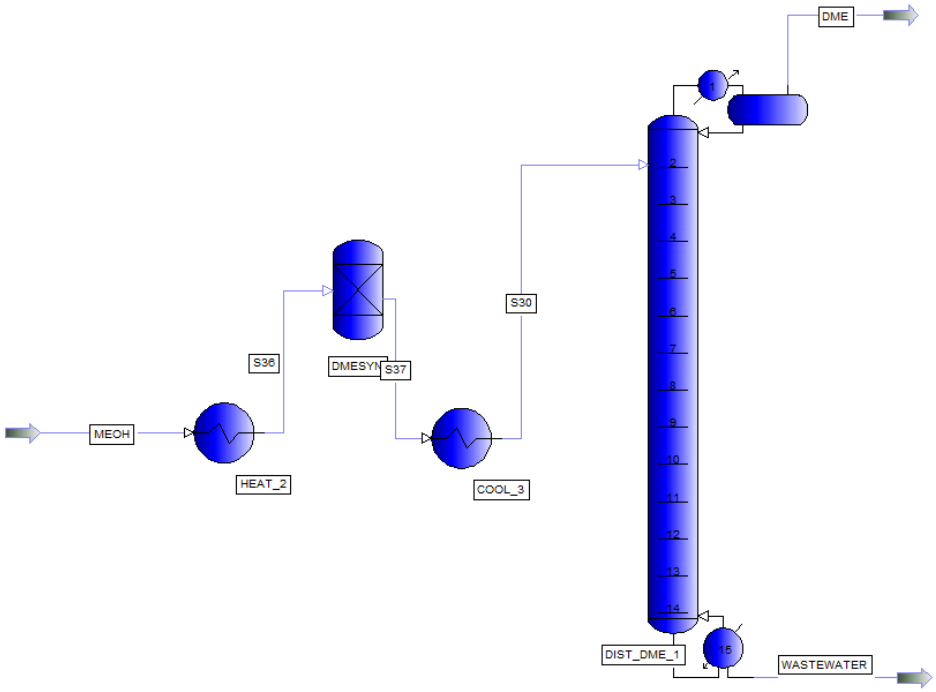


Figure D.4. The flowsheet of the simulation for the dimethyl ether from methanol process.

From the analysis of the process, this simple part of the process has a capital cost of 19.4 million USD and an operating cost of 10.5 million USD per year.

D.5 Ethylene carbonate synthesis

The ethylene carbonate is synthesized by reacting carbon dioxide with ethylene oxide. The flowsheet from the simulation is shown in Figure D.5. The stream table is provided in Table D.5.

From the analysis of the process, the capital cost is 52 million USD and the operating costs are 22.5 million USD per year. This process has the highest costs in the compression and separation of the ethylene carbonate.

Table D.4. The stream table of the simulation for dimethyl ether synthesis shown in Figure D.4.

Stream Name		DME	MEOH	S30	S36	S37	WASTEWATER
Stream Description							
Stream Phase		Vapor	Liquid	Mixed	Vapor	Vapor	Liquid
Total Molar Rate	kg-mol/hr	301.702	612.000	612.000	612.000	612.000	310.298
Total Mass Rate	kg/hr	13869.002	19617.787	19617.787	19617.787	19617.787	5748.784
Total Molecular Weight		45.969	32.055	32.055	32.055	32.055	18.527
Temperature	C	39.254	132.000	110.000	270.000	270.000	169.389
Pressure	BAR	8.000	10.000	9.000	10.000	9.000	9.000
Total Molar Comp. Fractions							
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0065	0.0032	0.0032	0.0032	0.0032	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0027	0.0018	0.4898	0.0018	0.4898	0.9635
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0009	0.9950	0.0189	0.9950	0.0189	0.0365
DME		0.9900	0.0000	0.4880	0.0000	0.4880	0.0000
Total Weight Comp. Fractions							
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0062	0.0044	0.0044	0.0044	0.0044	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0010	0.0010	0.2753	0.0010	0.2753	0.9369
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0006	0.9946	0.0189	0.9946	0.0189	0.0631
DME		0.9922	0.0000	0.7014	0.0000	0.7014	0.0000

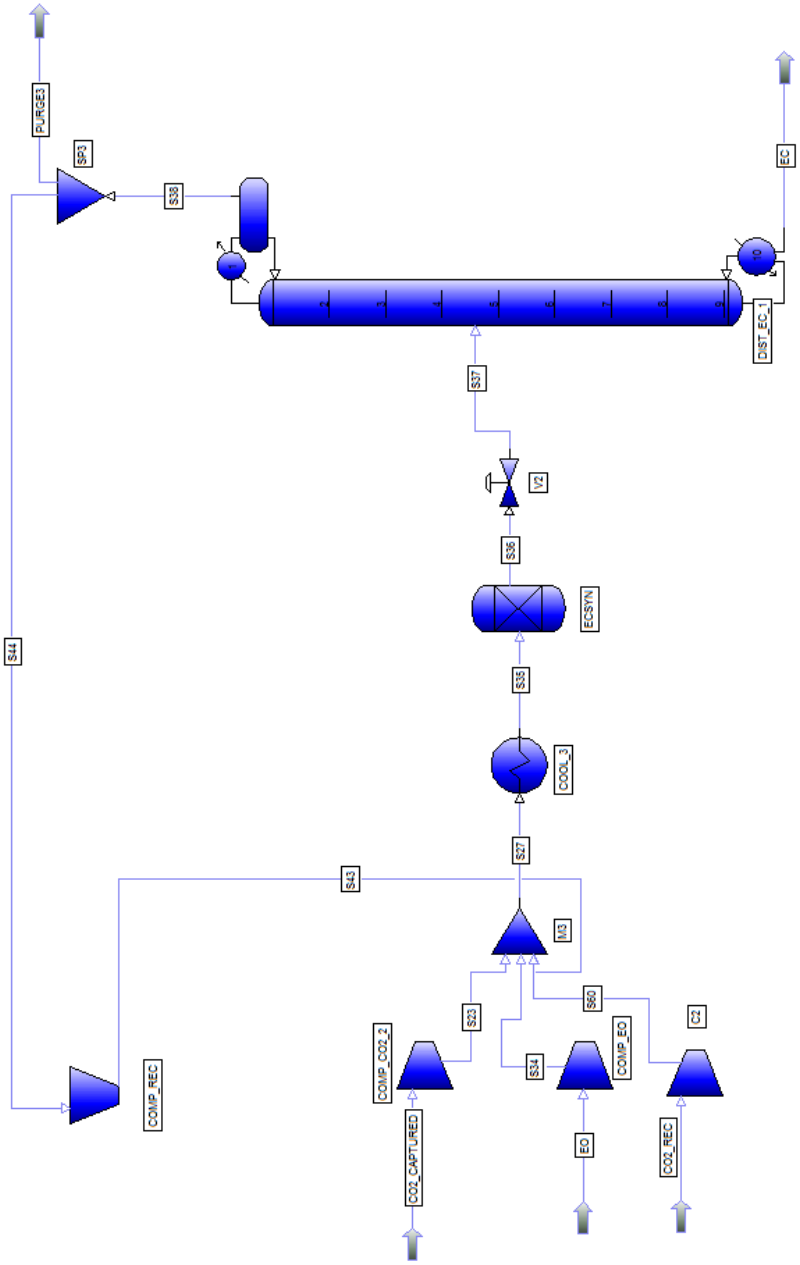


Figure D.5. The flowsheet of the simulation for the ethylene carbonate from carbon dioxide and ethylene oxide process.

Table D.5. The stream table of the simulation for ethylene carbonate synthesis shown in Figure D.5.

Stream Name		CO2_CAPTURED	CO2_REC	EC	EO	PURGE3	S23	S27	S34
Stream Description									
Stream Phase		Vapor	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor	Vapor
Total Molar Rate	kg-mol/hr	506.246	63.798	265.839	270.000	311.080	506.246	3639.816	270.000
Total Mass Rate	kg/hr	22279.768	2807.721	23293.497	11894.354	13690.738	22279.768	160200.923	11894.354
Total Molecular Weight		44.010	44.010	87.623	44.053	44.010	44.010	44.013	44.053
Temperature	C	96.316	-9.607	341.133	25.000	-25.510	688.017	293.819	367.638
Pressure	BAR	1.210	24.500	10.000	1.000	9.000	125.000	125.000	125.000
Total Molar Comp. Fractions									
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		1.0000	1.0000	0.0000	0.0000	0.9866	1.0000	0.9155	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0100	1.0000	0.0134	0.0000	0.0845	1.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.9900	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions									
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		1.0000	1.0000	0.0000	0.0000	0.9866	1.0000	0.9155	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0050	1.0000	0.0134	0.0000	0.0845	1.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.9950	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Stream Name		S35	S36	S37	S38	S43	S44	S60
Stream Description								
Stream Phase		Vapor	Mixed	Mixed	Vapor	Vapor	Vapor	Vapor
Total Molar Rate	kg-mol/hr	3639.816	3376.636	3376.636	3110.798	2799.718	2799.718	63.798
Total Mass Rate	kg/hr	160200.923	160200.880	160200.880	136907.382	123216.644	123216.644	2807.721
Total Molecular Weight		44.013	47.444	47.444	44.010	44.010	44.010	44.010
Temperature	C	110.000	110.000	47.810	-25.510	218.139	-25.510	141.531
Pressure	BAR	125.000	125.000	10.000	9.000	125.000	9.000	125.000
Total Molar Comp. Fractions								
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.9155	0.9089	0.9089	0.9866	0.9866	0.9866	1.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0845	0.0131	0.0131	0.0134	0.0134	0.0134	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0779	0.0779	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions								
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.9155	0.8432	0.8432	0.9866	0.9866	0.9866	1.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0845	0.0122	0.0122	0.0134	0.0134	0.0134	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.1447	0.1447	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

D.6 Dimethyl carbonate synthesis

The dimethyl carbonate process uses ethylene carbonate and methanol. The synthesis of of the dimethyl carbonate is provided from literature information on the conversion using immobilized ionic liquid (Kim et al., 2010). Subsequently, the product separation is performed using a series of distillation columns. From the analysis of the mixture behavior, the methanol/dimethyl carbonate mixture can be separated using different pressures in the distillation. The ethylene carbonate/ethylene glycol mixture cannot be separated conventionally. Therefore, water is added, which reacts with the ethylene carbonate to produce ethylene glycol and carbon dioxide. The resulting mixture can then be easily separated and the carbon dioxide is recycled. The simulation flowsheet is shown in Figure D.6 with the stream information in Table D.6.

The dimethyl carbonate part of the process is also analyzed. The capital costs are 68 million USD and the operating costs are 81.8 million USD per year. The dimethyl carbonate purification columns are energy intensive. In this process, they both account for 75% of the energy consumption. Therefore, the reduction of the energy consumption is targeted.

D.7 CCU: Dimethyl ether synthesis

There are two carbon dioxide capture and conversion processes to produce dimethyl ether: (1) dimethyl ether via methanol from combined reforming and (2) dimethyl ether via methanol from direct hydrogenation. The first is comprised of capture, methanol via combined reforming and dimethyl ether synthesis. Similarly, the second is comprised of capture, methanol via direct hydrogenation and dimethyl ether from methanol synthesis. The flowsheets and the proII simulation are shown in Section 4.2.1. The corresponding stream tables are provided here (Tables D.7 and D.8) and the simulation and analysis files are provided digitally.

D.8 CCU: Dimethyl carbonate synthesis

There are two carbon dioxide capture and conversion processes to produce dimethyl carbonate: (1) dimethyl carbonate via ethylene carbonate and methanol from combined reforming and (2) dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation. The first is comprised of capture, ethylene carbonate synthesis, methanol via combined reforming, and dimethyl carbonate synthesis from ethylene carbonate and methanol. Similarly, the second is comprised of capture, ethylene carbonate synthesis, methanol via direct hydrogenation, and

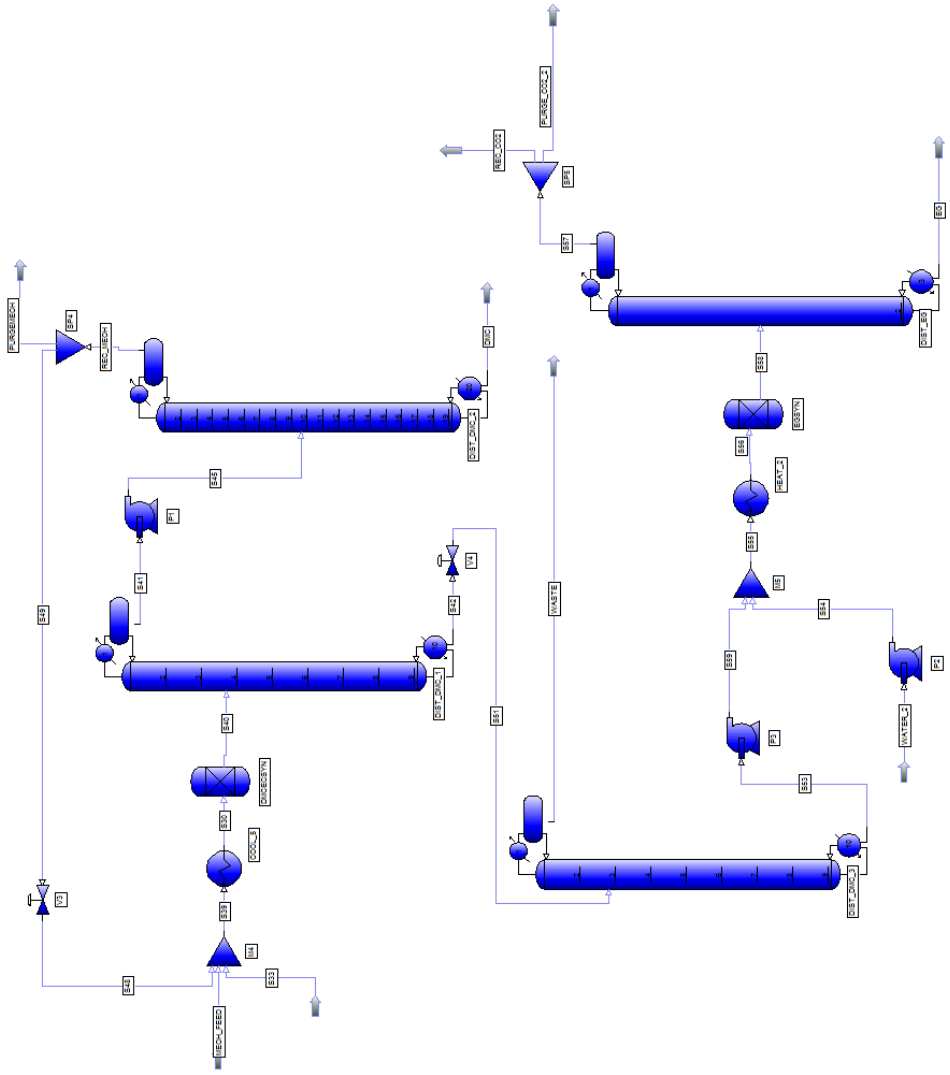


Figure D.6. The flowsheet of the simulation for dimethyl carbonate synthesis via ethylene carbonate and methanol process (adapted from Kongpanna et al. (2016)).

Table D.6. The stream table of the simulation for dimethyl carbonate shown in Figure D.6.

Stream Name		DMC	EG_FEED	EG	MEOH_FEED	PURGE_CO2_2	PURGEMEOH	REC_CO2	REC_MEOH	S30	S39	S40	S41	S42
Stream Description														
Stream Class		Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Vapor	Vapor	Liquid	Mixed	Mixed	Liquid	Liquid
Total Molar Rate	kg-mol/hr	153.261	265.939	258.411	1323.238	7.099	963.300	63.796	2752.286	3378.055	3378.055	3188.866	2905.848	283.018
Total Mass Rate	kg/hr	13713.773	23293.497	16006.042	42443.471	311.969	32449.427	2807.723	92712.650	125998.992	125998.992	125999.011	106426.423	19572.588
Total Molecular Weight		89.480	87.623	61.940	32.075	44.010	33.686	44.010	33.686	37.299	37.299	39.515	36.629	69.157
Temperature	C	21.000	34.133	32.235	10.338	24.507	18.015	24.507	18.015	10.000	145.146	10.000	124.553	241.041
Pressure	BAR	21.000	10.000	10.000	10.000	24.500	19.000	24.500	19.000	10.000	10.000	10.000	9.000	10.000
Total Molar Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.0000	0.0004	0.0000	1.0000	0.0000	1.0000	0.0047	0.0045	0.0045	0.0045	0.0054	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0015	0.0000	0.0028	0.0003	0.0000	0.0000	0.0000	0.0000	0.0001	0.0001	0.0021	0.0001	0.0007
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0001	0.0000	0.0002	0.0000	0.0002	0.0001	0.0001	0.0001	0.0002	0.0000
H2		0.0000	0.0000	0.0000	0.9990	0.0000	0.9953	0.0000	0.9953	0.9914	0.9914	0.8861	0.9949	0.0275
METHANE		0.0084	0.0000	0.0000	0.0000	0.0000	0.0023	0.0000	0.0023	0.0022	0.0022	0.0020	0.0026	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.9900	0.0000	0.0000	0.0000	0.0000	0.0289	0.0000	0.0289	0.0142	0.0142	0.0745	0.0077	0.0420
ETLNCARB		0.0000	0.9900	0.0028	0.0000	0.0000	0.0000	0.0000	0.0000	0.0779	0.0779	0.0231	0.0000	0.2604
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.0000	0.0031	0.0047	1.0000	0.0061	1.0000	0.0061	0.0045	0.0045	0.0045	0.0053	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0006	0.0000	0.0011	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0012	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0001	0.0000	0.0001	0.0000	0.0001	0.0001	0.0001	0.0001	0.0001	0.0000
H2		0.0000	0.0000	0.0000	0.9980	0.0000	0.9653	0.0000	0.9653	0.9614	0.9614	0.8581	0.9749	0.0275
METHANE		0.0048	0.0000	0.0000	0.0000	0.0000	0.0023	0.0000	0.0023	0.0022	0.0022	0.0020	0.0026	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0100	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.9946	0.0000	0.0000	0.0000	0.0000	0.0289	0.0000	0.0289	0.0142	0.0142	0.0745	0.0077	0.0420
ETLNCARB		0.0000	0.9900	0.0028	0.0000	0.0000	0.0000	0.0000	0.0000	0.0779	0.0779	0.0231	0.0000	0.2604
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Stream Name		DMC	EG_FEED	EG	MEOH_FEED	PURGE_CO2_2	PURGEMEOH	REC_CO2	REC_MEOH	S30	S39	S40	S41	S42
Stream Description														
Stream Class		Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Vapor	Vapor	Liquid	Mixed	Mixed	Liquid	Liquid
Total Molar Rate	kg-mol/hr	153.261	265.939	258.411	1323.238	7.099	963.300	63.796	2752.286	3378.055	3378.055	3188.866	2905.848	283.018
Total Mass Rate	kg/hr	13713.773	23293.497	16006.042	42443.471	311.969	32449.427	2807.723	92712.650	125998.992	125998.992	125999.011	106426.423	19572.588
Total Molecular Weight		89.480	87.623	61.940	32.075	44.010	33.686	44.010	33.686	37.299	37.299	39.515	36.629	69.157
Temperature	C	21.000	34.133	32.235	10.338	24.507	18.015	24.507	18.015	10.000	145.146	10.000	124.553	241.041
Pressure	BAR	21.000	10.000	10.000	10.000	24.500	19.000	24.500	19.000	10.000	10.000	10.000	9.000	10.000
Total Molar Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0044	0.0047	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	0.2187	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0001	0.0000	0.0000	0.0007	0.0001	1.0000	0.0239	1.0000	0.0000	0.0000	0.0022	0.0001	1.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0002	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0023	0.0023	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.9149	0.9653	0.0000	0.0275	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2343	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0026	0.0026	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0750	0.0289	0.0000	0.0289	0.0000	0.0289	0.0000	0.0289	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0077	0.0289	0.0000	0.0426	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.4481	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0053	0.0061	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	0.1858	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0007	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0021	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0102	0.0127	0.0000	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0019	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0036	0.0036	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.1910	0.0716	0.0000	0.0547	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Stream Name		S45	S46	S49	S51	S53	S54	S55	S56	S57	S58	S59	WASTE	WATER_2
Stream Description														
Stream Class		Liquid	Vapor	Vapor	Mixed	Liquid	Liquid	Liquid	Liquid	Vapor	Mixed	Liquid	Liquid	Liquid
Total Molar Rate	kg-mol/hr	2905.848	1788.966	283.018	283.018	256.377	72.720	329.397	329.397	70.886	329.397	256.577	25.441	72.720
Total Mass Rate	kg/hr	106426.423	60263.222	19572.588	19572.588	17916.653	1310.071	19125.724	19125.724	3119.692	19125.734	17916.653	1766.934	1310.071
Total Molecular Weight		36.629	33.686	69.157	69.157	69.436	18.015	58.060	58.060	44.010	58.061	69.436	69.447	18.015
Temperature	C	124.553	163.554	206.753	206.753	223.501	25.721	204.755	250.000	9.607	250.000	224.723	73.909	24.853
Pressure	BAR	20.000	10.000	2.000	2.000	2.000	30.000	30.000	30.000	24.500	30.000	30.000	1.000	1.000
Total Molar Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0044	0.0047	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2187	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0001	0.0000	0.0000	0.0007	0.0001	1.0000	0.2239	1.0000	0.0022	0.0001	0.0001	0.0084	1.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0002	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0023	0.0023	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.9149	0.9653	0.0000	0.0275	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2343	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0026	0.0026	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0750	0.0289	0.0000	0.0289	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0077	0.0289	0.0000	0.0426	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.4481	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions														
N2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0053	0.0061	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0000	0.0000	0.0002	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0001	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0021	0.0021	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0102	0.0127	0.0000	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0019	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0036	0.0036	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.1910	0.0716	0.0000	0.0547	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table D.7. The stream table of the simulation of combined capture and conversion to dimethyl ether via methanol from combined reforming shown in Figure 4.8.

Table D.8. The stream table of the simulation of combined capture and conversion to dimethyl ether via methanol from direct hydrogenation shown in Figure 4.9.

dimethyl carbonate synthesis from ethylene carbonate and methanol. The flowsheets and stream tables are provided here for the route via methanol from combined reforming (Figure D.7 and Tables D.9 and D.10) and the route via methanol from direct hydrogenation (Figure D.8 and Tables D.11 and D.12). The simulation and analysis files are provided digitally.

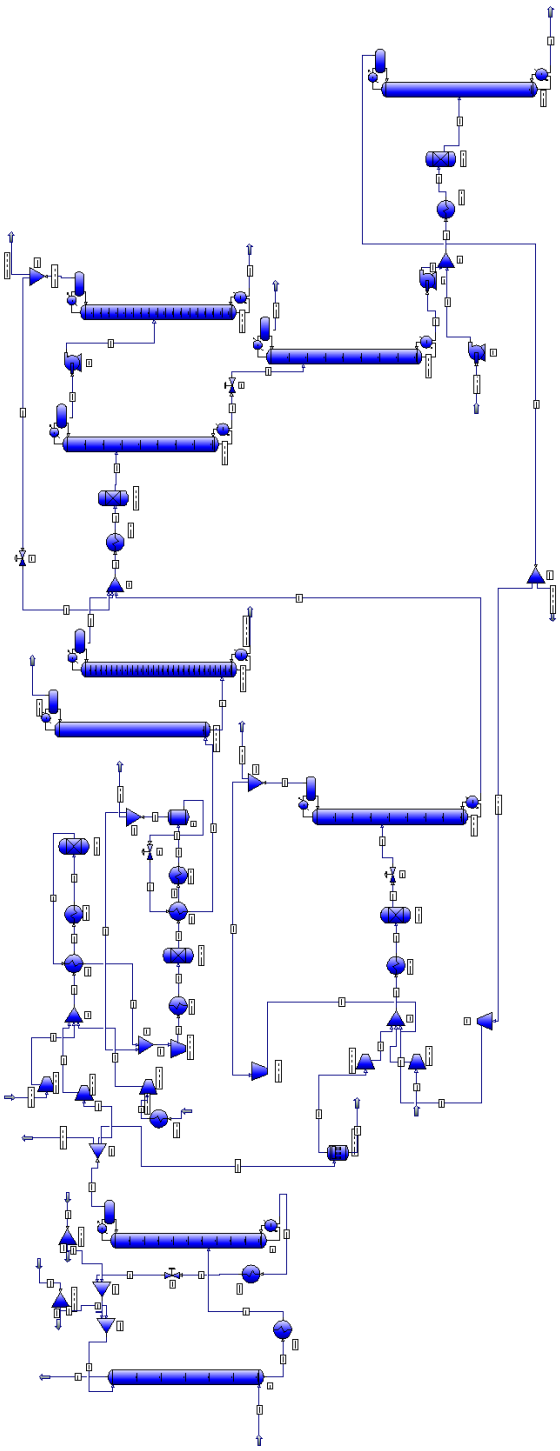


Figure D.7. The flowsheet of the simulation for carbon dioxide capture and conversion to dimethyl carbonate via ethylene carbonate and methanol from combined reforming.

Table D.9. Part 1 of the stream table of the CCU simulation for dimethyl carbonate with methanol from combined reforming shown in Figure D.7.

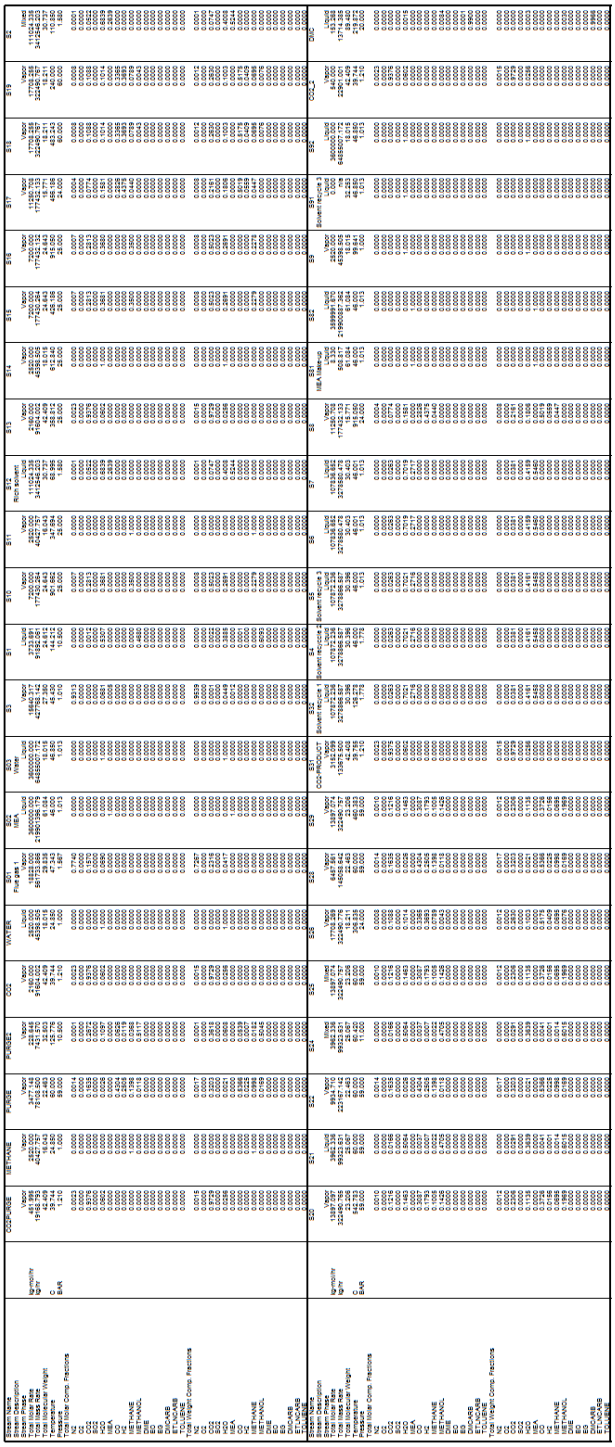
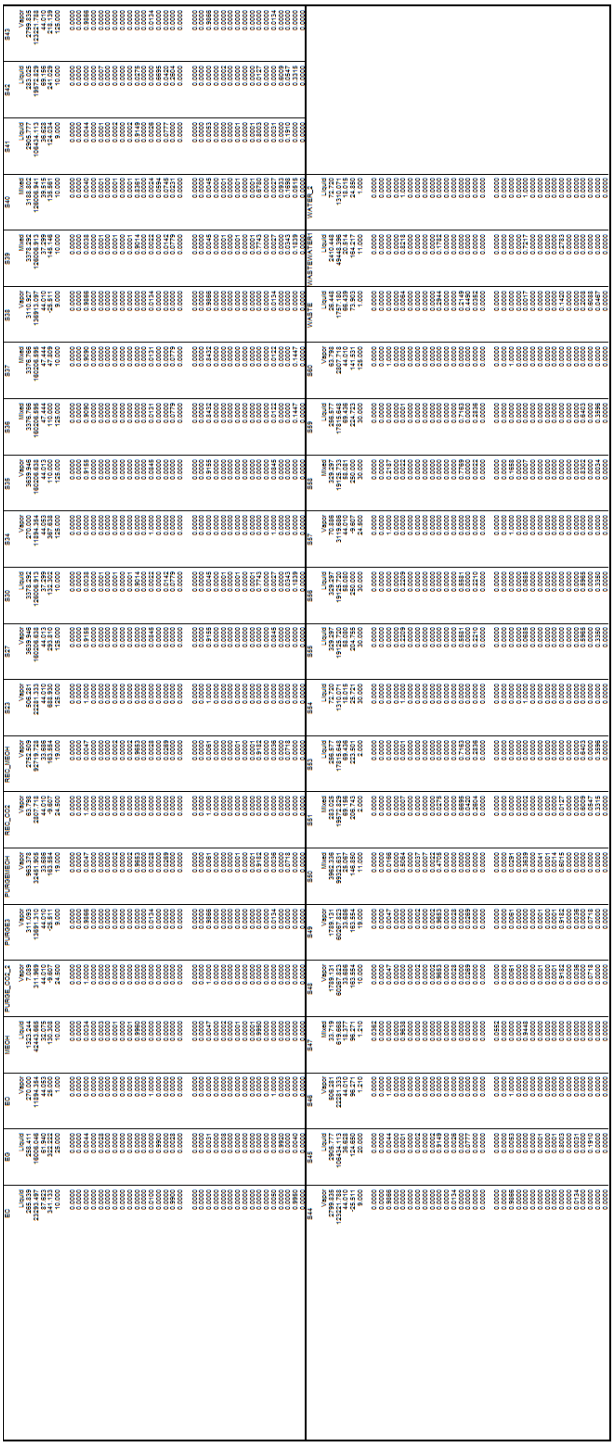


Table D.10. Part 2 of the stream table of the CCU simulation for dimethyl carbonate with methanol from combined reforming shown in Figure D.7.



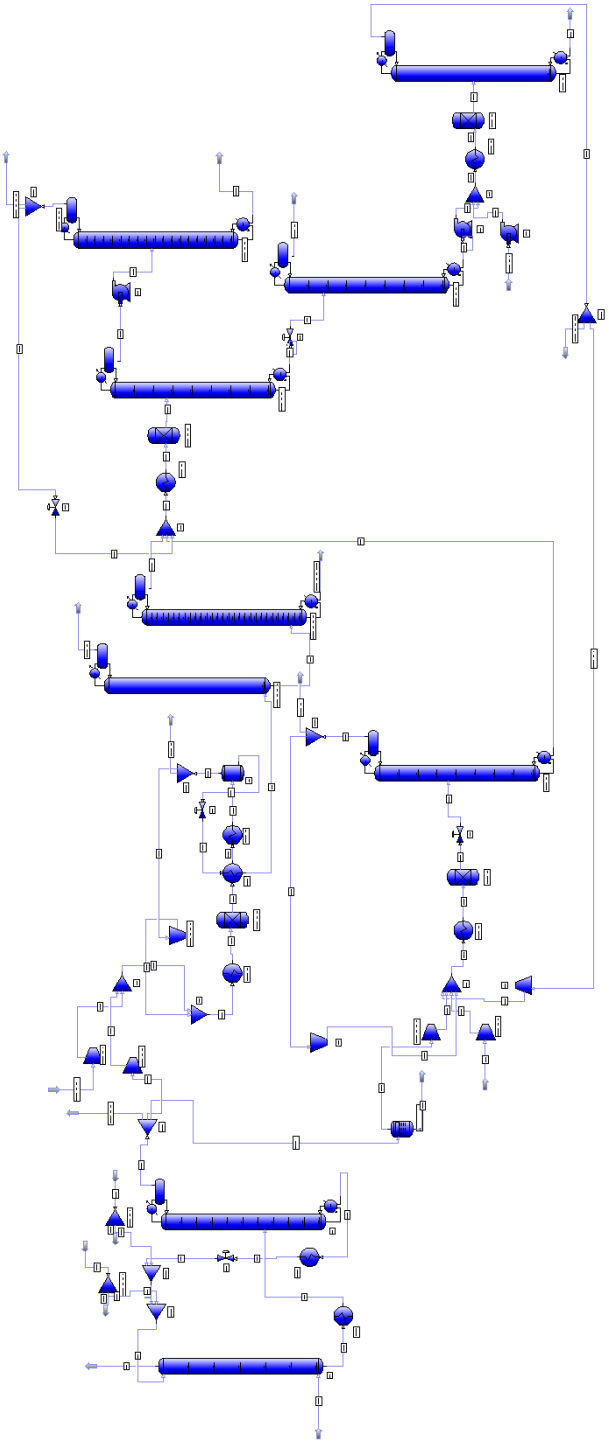


Figure D.8. The flowsheet of the simulation for carbon dioxide capture and conversion to dimethyl carbonate via ethylene carbonate and methanol from direct hydrogenation.

Table D.11. Part 1 of the stream table of the CCU simulation for dimethyl carbonate with methanol via direct hydrogenation shown in Figure D.8.

Stream Name		CO2PURGE	HYDROGEN	PURGE	PURGE2	CO2	S01	S02	S03	S1	S11	S12	S13	S15	S18	S19	S2	S20	S21	S22
Stream Description							Flue gas 1	MEA	Water			Wash solvent								
Stream Phase		Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Liquid	Liquid	Vapor	Liquid	Liquid	Vapor	Vapor	Vapor	Vapor	Mixed	Vapor	Liquid	Vapor
Total Molar Flow	kg-mol/hr	333.797	6046.000	2056.574	79.302	2160.000	18800.000	3000000.000	3600000.000	15895.203	3065.887	53433.656	2160.000	2526.000	15529.273	26267.297	53433.656	23196.746	3151.169	20990.740
Total Mass Flow	kg/hr	14452.215	12193.143	27267.914	2929.724	95040.000	581233.695	183000.000	64860000.000	438567.313	134215.313	1724662.250	95040.000	152153.953	247422.203	333144.406	1724662.250	333144.406	79243.742	2714418.703
Total Molecular Weight		43.308	2.016	13.700	36.945	43.333	30.918	18.015	18.015	27.577	43.764	32.261	43.333	12.281	13.444	32.261	32.261	15.325	24.989	34.703
Temperature	C	25.132	24.850	50.000	120.562	25.132	47.143	46.000	46.850	53.734	144.434	582.343	76.134	332.801	169.984	240.000	110.850	345.629	34.000	60.000
Pressure	BAR	1.210	1.100	24.000	10.000	1.210	1.067	1.013	1.013	1.013	10.000	20.000	1.458	20.000	10.000	20.000	1.458	10.000	24.000	24.000
Total Molar Comp. Fractions																				
N2		0.0013	0.0000	0.0014	0.0001	0.0013	0.7740	0.0000	0.0000	0.9166	0.0000	0.0000	0.0013	0.0000	0.0014	0.0000	0.0000	0.0001	0.0000	0.0014
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.9723	0.0000	0.4233	0.9723	0.9987	0.1570	0.0000	0.0000	0.0834	0.0915	0.0000	0.9723	0.2559	0.2541	0.0000	0.1103	0.2227	0.0116	0.2533
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2S		0.0264	0.0000	0.0027	0.0682	0.0264	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0264	0.0069	0.0069	0.0027	0.0001	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.2798	0.0000	0.0000	0.0000
O2MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	1.0000	0.9316	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.7168	0.7077	0.9316	0.0000	0.0000	0.0000	0.1077
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.7168	0.0000	0.8133	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E0		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DIUCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHYLCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions																				
N2		0.0029	0.0000	0.0014	0.0001	0.0009	0.7257	0.0000	0.0000	0.8434	0.0000	0.0000	0.0009	0.0000	0.0029	0.0000	0.0000	0.0023	0.0000	0.0029
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0116	0.0000	0.0034	0.0036	0.0116	0.0036	0.0000	0.0000	0.0046	0.0041	0.0000	0.0116	0.0046	0.0046	0.0000	0.0049	0.0023	0.0003	0.0116
H2O		0.0110	0.0000	0.0075	0.0466	0.0110	0.0417	0.0000	1.0000	0.0046	0.0796	0.0000	0.0110	0.0097	0.0075	0.0000	0.0075	0.0046	0.0066	0.0075
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E0		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DIUCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHYLCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Stream Name		S24	S25	S26	S29	S31	S32	S33	S4	S5	S6	S7	S8	S81	S82	CO2_2	DMC	EC	E3	E0
Stream Description						CO2-PRODUCT	Solvent recycle 1		Solvent recycle 2	Solvent recycle 3			MEA Make-up		Water Make-up					
Stream Phase		Mixed	Vapor	Mixed	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Liquid	Liquid	Liquid	Vapor
Total Molar Flow	kg-mol/hr	3131.169	23196.837	16559.166	23196.837	3003.797	48999.966	48999.966	48999.966	49839.966	49839.966	49920.597	110.097	6747.752	3699999.913	16237.450	16237.450	266.539	266.539	2701.000
Total Mass Flow	kg/hr	78243.242	333139.939	247427.156	333139.939	131373.766	1939312.188	1939312.188	1939312.188	1939325.868	1939325.868	1998564.418	6747.752	121646.375	64833359.721	715.450	715.450	23393.389	19274.861	111994.394
Total Molecular Weight		24.988	14.360	14.944	14.360	43.738	39.573	39.573	39.573	38.902	38.902	40.031	61.318	18.024	17.523	44.063	44.063	87.762	72.307	41.459
Temperature	C	60.000	326.881	124.983	46.000	25.132	46.000	46.000	46.000	46.039	46.039	46.010	46.000	46.000	46.850	25.132	25.132	220.925	341.134	25.000
Pressure	BAR	11.000	24.000	24.000	1.210	1.210	1.178	1.178	1.178	1.013	1.013	1.013	1.013	1.013	1.013	1.210	1.210	20.000	10.000	1.000
Total Molar Comp. Fractions																				
N2		0.0000	0.0012	0.0011	0.0014	0.0013	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0013	0.0013	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0116	0.2227	0.2541	0.2227	0.9723	0.0574	0.0574	0.0574	0.0573	0.0573	0.0573	0.0000	0.0000	0.0000	0.9723	0.9723	0.0000	0.0046	0.0000
H2O		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	1.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.2960	0.2960	0.2960	0.2961	0.2961	0.2956	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
O2MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.8133	0.7168	0.7077	0.7168	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E0		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DIUCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHYLCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp. Fractions																				
N2		0.0000	0.0023	0.0029	0.0009	0.0023	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0029	0.0029	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0116	0.0000	0.0034	0.0036	0.0116	0.0036	0.0036	0.0036	0.0036	0.0036	0.0036	0.0000	0.0000	0.0000	0.0116	0.0116	0.0000	0.0000	0.0000
H2O		0.0110	0.0000	0.0075	0.0466	0.0110	0.0417	0.0000	1.0000	0.0046	0.0796	0.0000	0.0110	0.0097	0.0075	0.0000	0.0075	0.0046	0.0066	0.0075
H2S		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.8133	0.7168	0.7077	0.7168	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E0		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
E1		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DIUCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETHYLCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table D.12. Part 2 of the stream table of the CCU simulation for dimethyl carbonate with methanol via direct hydrogenation shown in Figure D.8.

	METOH	PURGE_CO2_2	PURGE3	PURGEMEOH	REC_CO2	RECL_METOH	S10	S14	S16	S17	S23	S27	S30	S34	S36	S37	S38	S39	S40
	Liquid	Vapor	Vapor	Vapor	Liquid	Vapor	Mixed	Liquid	Liquid	Liquid	Vapor	Vapor	Liquid	Vapor	Mixed	Mixed	Vapor	Mixed	Mixed
	1449.781	7.562	329.483	1079.231	63.471	3994.194	326.756	254.396	254.396	72.360	325.033	3823.953	4231.474	270.000	3823.953	3950.772	3294.934	4231.474	4041.995
	46478.328	3167.372	14231.119	38522.535	2783.348	118733.450	18977.759	17974.183	17974.183	1593.598	20106.342	168834.215	153812.542	11984.364	168834.215	168834.875	143511.106	153812.542	152972.371
	2.000	24.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	131.869	-10.982	-26.175	163.482	-10.982	163.482	223.546	223.546	0.000	25.571	606.977	283.666	133.384	367.638	133.500	46.866	-26.175	144.078	136.496
	10.000	24.500	9.000	19.000	24.500	19.000	2.000	2.000	25.000	25.000	725.000	125.000	10.000	725.000	125.000	10.000	9.000	10.000	10.000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0032	1.0000	0.8971	1.0000	1.0000	1.0000	0.2196	0.0000	0.0000	0.0000	0.0000	0.0000	0.0036	0.0000	0.0000	0.0000	0.0000	0.0036	0.0036
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0018	0.0000	0.0000	0.0000	0.0000	0.0000	0.0018	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0

Appendix E

Stage 3 results

In Stage 3 of the framework, more sustainable solutions are found by targeting the areas for improvement from Stage 2. In the application, this is done by using hybrid methods and process intensification. The energy intensive methanol distillation is replaced by a hybrid methanol distillation-membrane process. Then, the dimethyl carbonate process is improved by using reactive distillation. Details are provided in Section E.1 and Section E.2, respectively.

E.1 Methanol synthesis with hybrid distillation-membrane

As the analysis from Stage 2 showed, one of the areas that could be improved is the energy intensive methanol distillation. This is done by apply the method of Tula et al. (2017) for the design of hybrid distillation-membrane separation sequences. The flowsheet of the new distillation sequence is shown for methanol via direct hydrogenation in Figure E.1 and the stream table is provided in Table E.1.

The analysis of the hybrid process reveals an increase in capital costs for that section of the CCU process. However, the decrease in operating costs offsets this increase, resulting in an overall reduction of the production costs of methanol. In addition, the NetCO_2 is reduced.

E.2 Dimethyl carbonate synthesis with reactive distillation

In addition to the methanol process, the dimethyl carbonate process is energy intensive in the downstream processing. This is the result of the steps needed to separate the product mixture due to the presence of azeotropes. The base case design was translated to a phenomena-based flowsheet and alternatives were generated. The best flowsheet alternative that was generated, uses reactive distillation and is shown

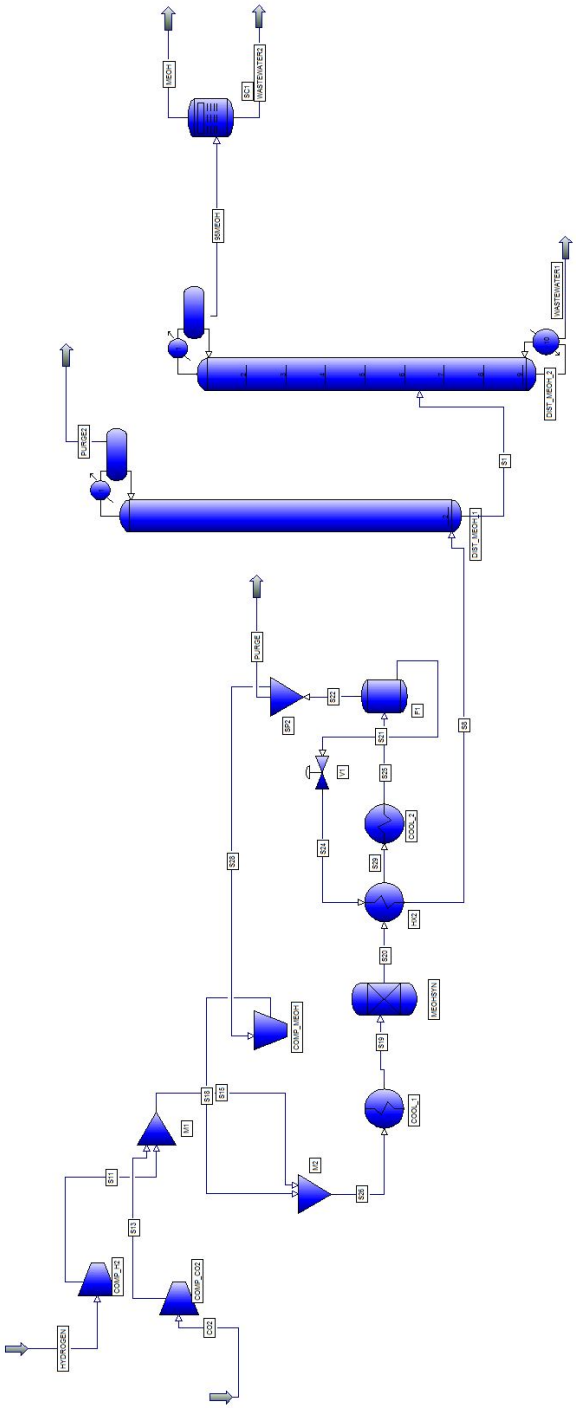


Figure E.1. The flowsheet of the simulation for methanol via direct hydrogenation with the hybrid distillation-membrane separation.

Table E.1. The stream table of the simulation for methanol via direct hydrogenation with the hybrid distillation membrane sequence shown in Figure E.1.

Stream Name		HYDROGEN	PURGE	PURGE2	CO2	S1	S11	S13	S15	S18	S19	S20
Stream Description												
Stream Phase		Vapor	Vapor	Vapor	Vapor	Liquid	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor
Total Molar Rate	kg-mol/hr	6120.000	1444.202	227.358	3030.139	3714.814	6120.000	3030.139	9150.139	8183.836	17333.975	13570.188
Total Mass Rate	kg/hr	12337.186	43638.844	8293.844	131213.420	91621.100	12337.186	131213.420	143350.606	247269.963	390620.570	390620.569
Total Molecular Weight		2.016	30.214	36.479	43.304	24.664	2.016	43.304	15.671	30.214	22.541	28.783
Temperature	K	333.150	333.150	366.483	298.333	416.483	852.483	298.333	743.556	432.227	513.145	664.038
Pressure	BAR	24.000	24.000	10.500	1.210	10.500	25.000	25.000	25.000	60.000	25.000	24.000
Total Molar Comp Fractions												
N2		0.0000	0.0027	0.0001	0.0013	0.0000	0.0000	0.0013	0.0004	0.0027	0.0015	0.0019
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.6398	0.4813	0.9723	0.0017	0.0000	0.9723	0.3223	0.6398	0.4720	0.4825
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0005	0.0005	0.0004	0.0575	0.0000	0.0004	0.0027	0.0005	0.0014	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0168	0.0011	0.0000	0.0000	0.0000	0.0000	0.0000	0.0168	0.0079	0.0120
H2		1.0000	0.3104	0.0063	0.0000	0.0000	1.0000	0.0000	0.6688	0.3104	0.4996	0.2204
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0242	0.4307	0.0000	0.4708	0.0000	0.0000	0.0000	0.0242	0.0114	0.1533
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp Fractions												
N2		0.0000	0.0025	0.0001	0.0008	0.0000	0.0000	0.0008	0.0008	0.0025	0.0019	0.0019
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.9019	0.8607	0.9682	0.0033	0.0000	0.9682	0.9022	0.9019	0.9214	0.7087
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0006	0.0007	0.0003	0.0383	0.0000	0.0003	0.0013	0.0006	0.0008	0.0008
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0156	0.0009	0.0000	0.0000	0.0000	0.0000	0.0000	0.0156	0.0099	0.0116
H2		1.0000	0.0207	0.0003	0.0000	0.0000	1.0000	0.0000	0.0859	0.0207	0.0447	0.0154
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0000	0.0257	0.3783	0.0000	0.6117	0.0000	0.0000	0.0000	0.0257	0.0162	0.1705
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
		S21	S22	S24	S25	S26	S28	S29	99/MEOH	S8	WASTEWATER1	
Stream Name												
Stream Description												
Stream Phase		Liquid	Vapor	Mixed	Mixed	Vapor	Vapor	Vapor	Liquid	Mixed	Liquid	Liquid
Total Molar Rate	kg-mol/hr	3940.172	8633.015	3940.172	13570.188	17333.975	8183.836	13570.188	1760.074	3940.172	1951.799	1951.799
Total Mass Rate	kg/hr	99914.944	260905.624	99914.944	390620.570	390620.569	247269.781	390620.569	53419.149	99914.944	36201.960	36201.960
Total Molecular Weight		25.345	30.214	25.345	28.800	22.547	30.214	28.800	31.434	25.345	18.548	18.548
Temperature	K	333.150	333.150	332.317	333.150	579.438	333.150	598.824	404.426	420.000	450.603	450.603
Pressure	BAR	24.000	24.000	11.000	24.000	25.000	24.000	24.000	10.000	11.000	11.000	11.000
Total Molar Comp Fractions												
N2		0.0000	0.0027	0.0000	0.0019	0.0015	0.0027	0.0019	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0000	0.6398	0.0004	0.4825	0.4720	0.6398	0.4825	0.0004	0.0004	0.0004	0.0004
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0000	0.0005	0.0000	0.0000	0.0014	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0000	0.0168	0.0000	0.0000	0.0000	0.0168	0.0000	0.0000	0.0000	0.0000	0.0000
H2		0.0004	0.3104	0.0004	0.2204	0.4996	0.3104	0.2204	0.0000	0.0004	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.0496	0.0242	0.0496	0.1533	0.0114	0.0242	0.1533	0.9500	0.0496	0.0096	0.0096
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Total Weight Comp Fractions												
N2		0.0000	0.0025	0.0000	0.0016	0.0025	0.0016	0.0016	0.0000	0.0000	0.0000	0.0000
O2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO2		0.0510	0.9019	0.0510	0.7067	0.9214	0.9019	0.7067	0.0050	0.0510	0.0510	0.0510
SO2		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
H2O		0.0036	0.0006	0.0036	0.0038	0.0089	0.0006	0.0038	0.0266	0.0036	0.0344	0.0344
MEA		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
CO		0.0001	0.0156	0.0001	0.0116	0.0099	0.0156	0.0116	0.0000	0.0001	0.0000	0.0000
H2		0.0000	0.0207	0.0000	0.0154	0.0447	0.0207	0.0154	0.0000	0.0000	0.0000	0.0000
METHANE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
METHANOL		0.5923	0.0257	0.5923	0.1705	0.0162	0.0257	0.1705	0.9604	0.5923	0.0656	0.0656
DME		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EO		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
EG		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
DMCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
ETLNCARB		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
TOLUENE		0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

in Figure E.2. The process is designed in Aspen with the resulting stream table in Table E.2.

The intensified alternative greatly reduces the amount of equipment in this part of the carbon dioxide capture and conversion processes. As a result, the capital costs are greatly reduced. In addition, as there are no longer as many distillation columns, the operating costs are also decreased, also resulting in a decrease in NetCO_2.

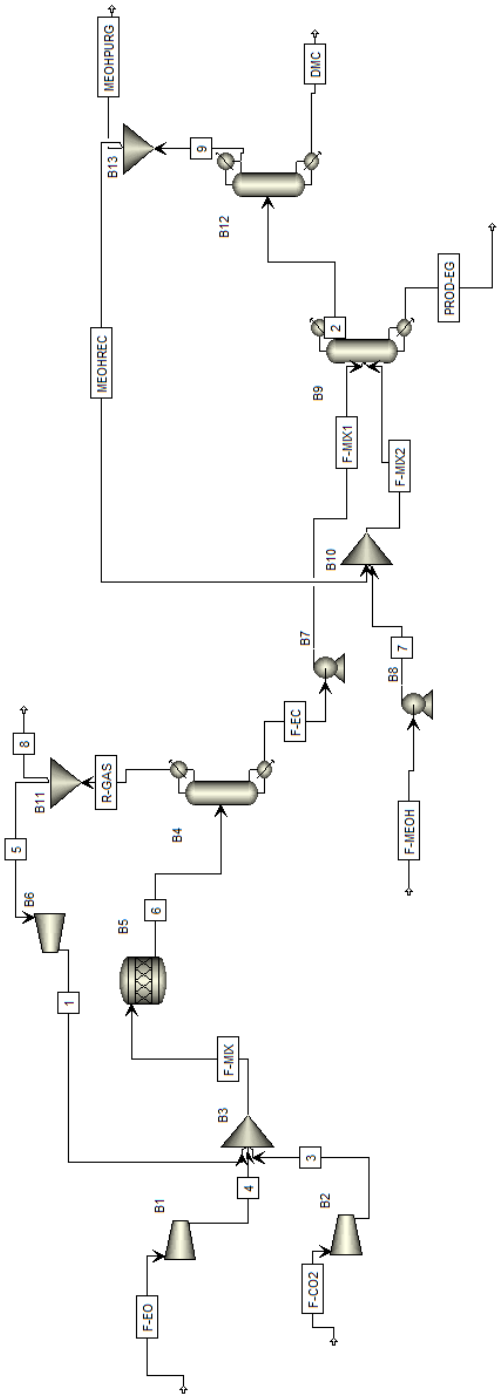


Figure E.2. The flowsheet of the simulation for dimethyl carbonate with reactive distillation.

Table E.2. The stream table of the simulation of the intensified reactive distillation process for dimethyl carbonate shown in Figure E.2.

	1	2	3	4	5	6	7	10 F-CO2	F-EC	F-EO	F-MEOH	F-MIX	F-MIX2	PROD-DMC	PROD-EG	R-GAS
Temperature C	746.1	198.2	623	362.1	248.1	110	25.1	155.2	25	248	25	25	577.8	25.1	89.5	292.7	132.7
Pressure bar	125	10	125	125	10	125	10	1	1	1	1	1	125	10	1	10	1
Vapor Frac	1	0	1	1	0	0.268	0	0	1	0	1	0	1	0	0	0	1
Mole Flow kmol/hr	139.68	80	77.04	77.04	77	216.72	150	8	77.04	77	77.04	150	293.76	150	72	72.39	139.72
Mass Flow kg/hr	6313.491	7006.425	3390.515	3393.855	6780.848	13097.861	4806.324	528.55	3390.515	6780.848	3393.855	4806.324	13097.861	4806.324	6477.874	4485.827	6317.013
Volume Flow cum/hr	94.666	9.009	45.919	32.551	6.155	24.502	6.063	0.542	1909.758	6.155	1909.758	6.062	166.279	6.063	6.829	5.403	4714.134
Enthalpy MMkcal/hr	-10.875	-10.725	-6.729	-0.531	-9.803	-22.405	-8.547	-0.876	-7.241	-9.803	-0.968	-8.548	-18.135	-8.547	-10.252	-7.058	-12.026
Mass Flow kg/hr																	
CARBO-01	5411.445		3390.515		trace	5411.445			3390.515	trace			8801.96				5411.445
ETHYL-01	570.929			3393.855	trace	570.929				trace	3393.855		3964.784				570.929
ETHYL-02	331.117	0.145			6780.848	7115.487		0.145		6780.848			331.117		trace	0.028	334.639
METHA-01		4.307					4806.324	trace				4806.324		4806.324	4.307	7.809	
DIMET-01		6576.347						102.78							6473.567	0.003	
ETHYL-03		425.625						425.625							< 0.001	4477.987	
Mole Flow kmol/hr																	
CARBO-01	122.96		77.04		trace	122.96			77.04	trace			200				122.96
ETHYL-01	12.96			77.04	trace	12.96				trace	77.04		90				12.96
ETHYL-02	3.76	0.002			77	80.8		0.002		77			3.76		trace	< 0.001	3.8
METHA-01		0.134					150	trace				150		150	0.134	0.244	
DIMET-01		73.007						1.141							71.866	< 0.001	
ETHYL-03		6.857						6.857							trace	72.146	
Mole Frac																	
CARBO-01	0.88		1		trace	0.567			1	trace			0.681				0.88
ETHYL-01	0.093			1	trace	0.06				trace	1		0.306				0.093
ETHYL-02	0.027	21 PPM			1	0.373		207 PPM		1			0.013		trace	4 PPM	0.027
METHA-01		0.002					1	3 PPB			1			1	0.002	0.003	
DIMET-01		0.913						0.143							0.998	516 PPB	
ETHYL-03		0.086						0.857							7 PPB	0.997	

Appendix F

Digital appendix

In addition to the written thesis, there is a digital appendix, organized in the subsequent manner, which contains any necessary files and electronic data that is not included in the written thesis.

Digital thesis This folder contains the PDF of the thesis along with the Latex files, including figures, that are used to compile it.

Papers This folder contains the different publications that were written during the PhD divided into the 7 folders for the journal or proceedings they are included in.

Reaction path synthesis (RPS) This folder contains all the information for the reaction path synthesis performed. It is subdivided in to three further folders for the tools used, the results from the tools, and the database.

Simulation library This is the library of all the simulations organized by product and type.

Stage 1 This contains all the results for Stage 1 and all the Scenarios considered, including input and output files.

Stage 2 This folder has all the results for Stage 2 for the four processes considered, including simulation files and analysis results.

Stage 3 The contains the results for Stage 3 for the improved methanol and dimethyl carbonate processes.

Superstructure database This folder contains the superstructure database.

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